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ON
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JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Catalytic Reduction of Unsaturated Organic Compounds. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1074—1077).—In the hydrogenation of unsaturated compounds by hydrogen in the presence of metallic hydroxides, complex intermediate compounds are formed of the type

$$\begin{matrix} R^1\cdot CH\cdot CH\cdot R^2 \\ \diagdown\ \diagup \\ H_nM(OH)_m \end{matrix}$$

. These complex compounds yield colloidal solutions, and owing to their continuous formation and decomposition into $R^1CH_2\cdot CH_2R^2 + M(OH)_m$, they constitute the true carriers of the active hydrogen. Z. K.

The Systems Aluminium Bromide and Ethylene Dibromide. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1308—1310).—Aluminium bromide dissolves readily in ethylene bromide, the saturated solution depositing small crystals. The solubility curve is characteristic for the case where the components form no chemical compound. The eutectic point lies at 2° at the approximate composition $AlBr_3,3\cdot37C_2H_4Br_2$. Z. K.

***n*-Butylhexylcarbinol.** SERGIUS BYRTSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 876—879).—n-*Butylhexylcarbinol*, $C_{11}H_{24}O$, was obtained by Grignard's reaction by the action of magnesium

butyl iodide on heptaldehyde. It is a colourless liquid with an odour something like that of the juice of *Conium maculatum*. It has b. p. 223·5—225°/750·7 mm., 229·1—230·6° (corr.), D_0^0 0·8378, $D_0^{17·5}$ 0·8300, and solidifies at −3·5°. The *acetyl* derivative,

$$C_{13}H_{26}O_2,$$

b. p. 232·5—234°/747·7 mm., 239·3—240·8° (corr.), D_0^0 0·8677, $D_0^{17·5}$ 0·8562, has a faint pleasant odour, and solidifies at −1·5°. When oxidised with chromic mixture, the carbinol forms acids and n-*butyl hexyl ketone*, $C_{11}H_{22}O$, b. p. 218—221°/742 mm., 223·9—226·9° (corr.), D_0^0 0·8401, $D_0^{17·5}$ 0·8320, which is a liquid of pleasant odour and forms a *semicarbazone*, $C_{12}H_{25}ON_3$, m. p. 64·5°. Z. K.

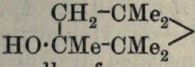
Action of Magnesium Amalgam on Acetone. βγε-Trimethylhexan-βγε-triol and Some of its Derivatives. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Ann. Chim. Phys.*, 1910, [viii], 21, 407—419, 425—432).—A more detailed account of the results published already by Richard and Langlais (Abstr., 1910, i, 455), with further particulars regarding the course of the reaction. The products resulting from the treatment of acetone with magnesium amalgam are of two kinds: (1) those derived from 2 mols. of acetone, namely, pinacone, mesityl oxide, β-methylpentan-β-ol-δ-one (see below), and the glycol corresponding with the last-mentioned alcohol; and (2) those derived from 3 mols. of acetone, namely, *iso*phorone and βγε-trimethylhexan-βγε-triol. Of these, the third appears to be the most important intermediate product, since from it pinacone, the chief final product, and mesityl oxide appear to be formed by decomposition in the course of the reaction (compare Couturier and Meunier, Abstr., 1902, i, 335; 1905, i, 326).

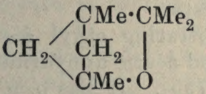
The dihydric alcohol, $C_6H_{14}O_2$, b. p. 102—103°/17 mm. or 188—190°/760 mm., previously referred to (Abstr., 1910, i, 456), furnishes a *diacetate*, b. p. 97—104°/17 mm., and when heated with pyruvic acid yields a *product*, $C_9H_{14}O_3$, m. p. 66°, b. p. 125—130°/17 mm., which crystallises in slender needles, and is provisionally regarded as a "dehydrated pyruvate." These reactions indicate that the dihydric alcohol is β-methylpentan-βδ-diol, and this is confirmed by its preparation by the reduction of β-methylpentan-β-ol-δ-one,

$$HO{\cdot}CMe_2{\cdot}CH_2{\cdot}COMe$$

(Heintz, this Journ., 1876, i, 365), which also occurs in the products of the action of magnesium amalgam on acetone; it has b. p. 75—80°/17 mm., and is readily decomposed on heating, especially in presence of an alkali. Dilute sulphuric acid converts it into mesityl oxide.

βγε-Trimethylhexan-βγε-triol, $OH{\cdot}CMe_2{\cdot}CMe(OH){\cdot}CH_2{\cdot}CMe_2{\cdot}OH$, already described (succeeding abstract, and Abstr., 1910, i, 456), is dealt with in detail in the second paper. On treatment with chromic acid, it is decomposed, yielding 1 mol. each of acetone and β-methylpentan-β-ol-δ-one (see above). When heated alone or with acids, the trihydric alcohol undergoes dehydration, and in the case of acetic anhydride or pyruvic acid furnishes an ester of the dehydrated product,

When heated alone, the alcohol loses $1H_2O$, giving a *substance* (a),  O, m. p. 77°, b. p. 75°/10 mm., which crystallises in needles from a mixture of light petroleum and ether, and this on boiling with 20% sulphuric acid is transformed into a *cyclic oxide* (b) (annexed formula), b. p. 126—127°, D^{25} 0·826, a mobile oil having a terpene-like odour. Both these products are formed when the trihydric alcohol is boiled with 20% hydrochloric acid, and (b) almost entirely when 20% sulphuric acid is used, although in this case a minute amount of an *isomeride* (?) of (a) is produced. This has b. p. 168°/760 mm. With a boiling saturated solution of oxalic acid, substance (a) only is formed. Boiling acetic anhydride converts the trihydric alcohol into a *dehydrated monoacetate*, $C_{11}H_{20}O_3$, b. p. 89°/17 mm., D_4^0 0·989, which appears to be the acetyl derivative of substance (a), since it is also formed by the acetylation of the latter.



Pyruvic acid heated with the alcohol yields a substance (b) in small quantity, and in addition a *dehydrated pyruvate*, $C_{12}H_{18}O_3$, m. p. 122°, b. p. 140°/13 mm., which crystallises in needles, and is probably the pyruvate of substance (a), since it is also produced from this by the action of pyruvic acid. T. A. H.

Synthesis of $\beta\zeta$-Dimethylheptan-$\beta\delta\zeta$-triol and of $\beta\gamma\epsilon$-Trimethylhexan-$\beta\gamma\epsilon$-triol. II. LOUIS BOUVEAULT and FERDINAND LEVALLOIS (*Ann. Chim. Phys.*, 1910, [viii], 21, 419—425).—This work was undertaken with a view to the determination of the constitution of the trihydric alcohol obtained by the action of magnesium amalgam on acetone (preceding abstract, and Richard and Langlais, Abstr., 1910, i, 455), which was at one time thought to be the first, but is now known to be the second, of the two substances synthesised.

$\beta\zeta$-Dimethylheptan-$\beta\delta\zeta$-triol,

$$OH{\cdot}CMe_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CMe_2{\cdot}OH,$$

m. p. 54°, b. p. 155—160°/18 mm., obtained by the interaction of magnesium methyl iodide with methyl β-hydroxyglutarate, is a colourless liquid of sweet taste, and somewhat resembles glycerol.

Methyl citramalate (α-methylmalate), which was used as the starting point for the preparation of the trihydric alcohol, is not easily obtained in good yield by Michael's process (Abstr., 1893, i, 146). For its preparation, ethyl acetoacetate was treated with anhydrous hydrogen cyanide in presence of triethylamine, and the resulting *nitrile*,

$$OH{\cdot}CMe(CN){\cdot}CH_2{\cdot}CO_2Et,$$

b. p. 133°/20 mm., saturated with dry hydrogen chloride in presence of excess of methyl alcohol, and the resulting imino-ether hydrochloride poured on ice, treated with potassium carbonate, and the methyl citramalate, b. p. 112°/15 mm., extracted with ether and purified by distillation. With magnesium methyl iodide, it furnished $\beta\gamma\epsilon$-trimethylhexan-$\beta\gamma\epsilon$-triol, $OH{\cdot}CMe_2{\cdot}CMe(OH){\cdot}CH_2{\cdot}CMe_2{\cdot}OH$, identical with that described already (preceding abstract, and Richard and Langlais, Abstr., 1910, i, 455). T. A. H.

Aliphatic Nitro-compounds. VIII. α-Nitropropionic Acid. WILHELM STEINKOPF and ALEXANDER SUPAN (*Ber.*, 1910, 43, 3239—3249. Compare Abstr., 1909, i, 559, 874).—Ethyl α-nitropropionate can be prepared by the action of concentrated alcoholic ammonia on ethyl nitro*iso*succinate; the first product is the ammonium salt of the *aci*-nitro-ester, m. p. 119° (decomp.), but this reacts with dilute sulphuric acid, yielding the free ester.

Ethyl nitro*iso*succinate is best prepared by nitrating ethyl *iso*-succinate with a mixture of fuming nitric acid and acetic anhydride (compare Bouveault and Wahl, Abstr., 1904, i, 795). It has b. p. 121—122°/11 mm., whereas Salway gives 108°/13 mm., and Ley and Hantzsch give 126—127°/10 mm. The yields obtained by methylating ethyl nitromalonate by Ulpiani's method (Abstr., 1903, i, 791) or by Purdie's method (Trans., 1899, 75, 157) are poor.

The *ammonium* salt of α-nitropropionamide, $C_3H_9O_3N_3$, formed by heating ethyl α-nitropropionate with concentrated alcoholic ammonia for two hours at 100°, crystallises from a mixture of alcohol and ether, and has m. p. 127—128°. The *amide*, $NO_2\cdot CHMe\cdot CO\cdot NH_2$, is best prepared by converting the ammonium salt into the insoluble lead salt, suspending this in dry ether, and passing in dry hydrogen sulphide at 0°. It crystallises from chloroform or ether in slender, colourless needles, m. p. 68—69°. Chlorine reacts with an ice-cold aqueous solution of the ammonium salt, yielding *α-chloro-α-nitropropionamide*, $NO_2\cdot CClMe\cdot CO\cdot NH_2$, which crystallises from water in glistening, colourless plates, m. p. 82°. The corresponding *bromo*-derivative, $C_3H_5O_3N_2Br$, has m. p. 89°. The *dipotassium* salt of α-nitropropionic acid, $C_3H_3O_4NK_2,EtOH$, is obtained as long needles when the ammonium salt of ethyl *aci*nitropropionate is boiled for fifteen minutes with an alcoholic solution of potassium hydroxide (20%). The corresponding *sodium* salt, $C_3H_3O_4NNa_2$, separates from a mixture of alcohol and water in long needles.

α-Nitropropionic acid, $NO_2\cdot CHMe\cdot CO_2H$, is obtained by suspending the silver salt in a small amount of water, and adding the theoretical amount of *N*-hydrochloric acid and extracting rapidly with ether, or by mixing a concentrated aqueous solution of the sodium salt with much ether, cooling in a freezing mixture, and shaking whilst the theoretical amount of *N*-hydrochloric acid is added. The ethereal solution is dried with phosphoric oxide and the ether removed. It crystallises from carbon disulphide in long, colourless needles, m. p. 61—61·5° (decomp.).

Nitroacetaldehydephenylhydrazone is formed by the action of an aqueous solution of benzenediazonium chloride on a not too dilute solution of sodium α-nitropropionate. It crystallises from alcohol in golden-yellow plates, m. p. 136·5°.

Nitroacetic acid can be obtained from its potassium salt in much the same manner as the nitropropionic acid from its sodium salt.

The conversion of ethyl nitro*iso*succinate into ethyl nitropropionate and then into nitropropionamide by means of ammonia supports Ratz's view regarding the mechanism of the reaction between ethyl nitromalonate and ammonia (compare Abstr., 1904, i, 857). J. J. S.

Ammonium Salts of Fatty Acids (Oleic, Palmitic, Stearic), and the Separation of the Saturated Fatty Acids (Palmitic and Stearic) from Oleic Acid. I. PIETRO FALCIOLA (*Gazzetta*, 1910, **40**, ii, 217—229).—The author has studied the composition and the solubilities (in some cases quantitatively) of the ammonium salts of the fatty acids mentioned, and has found that the oleate is soluble in cold alcohol, whilst the palmitate and stearate are not. The quantitative separation is effected by dissolving the mixture of acids in warm ether, passing ammonia through the solution, and allowing it to cool to the ordinary temperature. When almost all the ether has evaporated, the pasty residue is extracted with cold ammoniacal alcohol (at about 0°), filtered at the pump, and washed with a further portion of this solvent. From precipitate and filtrate the separated free fatty acids can be liberated by treatment with dilute hydrochloric acid. The methods gives results sufficiently accurate for technical analysis.

When concentrated aqueous ammonia is added to a warm alcoholic solution of stearic acid, *ammonium stearate*, $C_{18}H_{35}O_2\cdot NH_4$, separates as a crystalline precipitate on cooling. When heated, it undergoes change at 90°, and is completely melted at about 110° (with evolution of gas). It loses ammonia on keeping, and, after treatment with water, the crystals have the composition of the *acid* salt,

$$C_{18}H_{36}O_2,C_{18}H_{35}O_2\cdot NH_4.$$

The *palmitate*, $C_{16}H_{31}O_2\cdot NH_4$, is similarly prepared, and has similar properties. It softens towards 90°, and melts completely above 100° (with evolution of gas). Treatment with water converts it into the *acid* salt, $C_{16}H_{32}O_2,C_{16}H_{31}O_2\cdot NH_4$. The *oleate*, $C_{18}H_{33}O_2\cdot NH_4$, is prepared by passing ammonia into an ethereal solution of oleic acid. It loses ammonia when kept in the air. With water, it yields a gelatinous colloidal solution. R. V. S.

The Elaidin Reaction. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1068—1073).—From theoretical reasoning it seems probable that the elaidin reaction given with oleic acid by sulphurous and nitrous acids would also be given by many other substances, capable like these of internal re-grouping and existence in at least two forms of different configuration. Phosphoric and phosphorous acids both give the elaidin reaction with oleic acid when heated at 170—180° in a slow current of hydrogen and then in a sealed tube, the former acid reacting more rapidly than the latter. In the presence of phosphorus trichloride, the reaction is still slower.

Tetranitromethane and ethyl nitrite both convert oleic acid into elaidic acid, an additive compound of the nitromethane and unsaturated acid being formed, and gases also evolved in the former case. Elaidic acid when heated with phosphoric acid for thirty to forty hours at 180°, yields an oleic acid, which does not react with ethyl nitrite, is more stable than elaidic or ordinary oleic acid, and seems to be identical with the oleic acid obtained by the prolonged action of sunlight on the ordinary acid. Z. K.

The Optical Behaviour of Lactic Acid in a Meat Preparation. Ernst Salkowski (*Zeitsch. physiol. Chem.*, 1910, **69**, 471—473).—In an American meat-juice it was noticed that in time the sarcolactic acid passes more and more into an inactive modification of the acid. In the course of a year the change was almost complete. It is suggested that the cause is the presence of a large amount of potassium dihydrogen phosphate. W. D. H.

New Method for Preparation of Glycidic Esters. Georges Darzens (*Compt. rend.*, 1910, **151**, 883—884).—Ethyl α-chloro-β-hydroxy*iso*valerate is conveniently prepared by adding magnesium amalgam to a mixture in molecular proportions of acetone and ethyl dichloroacetate dissolved in benzene, the product being then treated with water. Esters of this type are readily converted into the corresponding glycidic esters; thus, on treating the foregoing compound with sodium ethoxide, a theoretical yield of ethyl ββ-dimethylglycidate is obtained. Although the condensation of ethyl dichloroacetate with ketones other than acetone has not been successful, yet this method of synthesising glycidic esters appears to be general, inasmuch as the required hydroxy-ester can always be obtained through the action of hypochlorous acid on the corresponding unsaturated acid. W. O. W.

Pinacolin Derivatives. A. Richard (*Ann. Chim. Phys.*, 1910, [viii], **21**, 325—406. Compare Abstr., 1910, i, 455, 458, 462).—This work was undertaken in order to ascertain what influence the ψ-butyl group has on the stability of the compounds in which it occurs, and particularly whether the unsymmetrical character of substances containing this group gives rise to any peculiar form of isomerism. The results obtained show that the alkyl chlorides containing this group allow of ready molecular transformation when they contain a hydrogen atom attached to the carbon, which carries the chlorine atom, but in no case was any isomerism noticed among the acids containing this group.

Methyl pivalate has D_4^0 0·891. The ethyl ester has D_4^0 0·875, and on reduction by Bouveault and Blanc's method (Abstr., 1903, i, 597) furnishes ββ-dimethylpropyl alcohol, $CMe_3{\cdot}CH_2{\cdot}OH$ (Tissier, Abstr., 1893, i, 542), m. p. 50°, b. p. 113—115°/760 mm. or 64°/100 mm., which yields a *phenylurethane*, m. p. 114°, and a *pyruvate*, b. p. 78—80°/23 mm., the *semicarbazone* of which is crystalline and melts at 166°. On saturation with dry hydrogen chloride, the alcohol yields the corresponding chloride, b. p. 87—90°, but this dissociates when heated into β-methyl-Δ^{β}-butylene and hydrogen chloride, and the former, when re-combined with hydrogen chloride and then transformed into the acetate and the latter hydrolysed, yields the isomeric *tert.*-alcohol, $CMe_2(OH){\cdot}CH_2Me$ (compare Tissier, *loc. cit.*). Magnesium ββ-dimethylpropyl chloride on treatment with oxygen furnishes an *alcohol*, m. p. −12°, b. p. 101—103°, D_4^0 0·827, possessing a camphoraceous odour, which on heating with pyruvic acid is not esterified, but is dehydrated, yielding β-methyl-Δ^{β}-butylene. Bouveault has shown that this reaction is characteristic of tertiary alcohols (Abstr.,

1904, i, 465). With phenylcarbimide, dehydration also occurs. With carbon dioxide, magnesium $\beta\beta$-dimethylpropyl chloride gives rise to $\beta\beta$-dimethylbutyric acid.

Pinacolin may be reduced by sodium in alcohol, potassium hydroxide in alcohol, or sodium in moist ether, giving in all cases good yields of pinacolyl alcohol (compare Friedel and Silva, this Journ., 1873, **26**, 488). The latter furnishes a *pyruvate*, b. p. 78—80°/17 mm., and the *semicarbazone* of this is crystalline and melts at 175°. The magnesium derivative of the chloride of this alcohol on treatment with oxygen yields dimethyl*iso*propylcarbinol, which confirms Couturier's observation that the chloride is unstable and on heating yields $\beta\gamma$-dimethyl-Δ^{β}-butylene. The present transformation may be represented thus :

$$CMe_3\cdot CMeHCl \longrightarrow CMe_2\colon CMe_2 \longrightarrow CMe_2Cl\cdot CHMe_2 \longrightarrow OH\cdot CMe_2\cdot CHMe_2.$$

With carbon dioxide, magnesium pinacolyl chloride furnishes *$\alpha\alpha\beta$-trimethylbutyric acid*, m. p. 50°, b. p. 106°/15 mm.

$\alpha\alpha\beta\beta$-Tetramethylpropyl chloride (Henry, Abstr., 1906, i, 477) reacts with magnesium methyl iodide, forming a product which on treatment with carbon dioxide gives $\beta\beta\gamma\gamma$-tetramethylbutane (*loc. cit.*, p. 473) and $\alpha\alpha\beta\beta$-tetramethylbutyric acid, $CMe_3\cdot CMe_2\cdot CO_2H$. This chloride is therefore much less liable to undergo intramolecular transformation than those described above, due to the fact that it contains no free hydrogen atom associated with the carbon carrying the chlorine atom.

Trimethylpyruvic acid, $CMe_3\cdot CO\cdot CO_2H$, prepared by Glücksmann's method (Abstr., 1890, i, 237), crystallises in the absence of moisture, and then melts at 125°. In moist air it absorbs $\frac{1}{2}H_2O$, and then has m. p. 90°. The *oxime*, m. p. 85°, crystallises in colourless spangles ; the *hydrazone*, $N_2\left(\colon C{<}{}^{CMe_3}_{CO_2H}\right)_2$, m. p. 207°, forms sulphur-yellow needles, and the *semicarbazone* has m. p. 195° (decomp.). The *methyl* ester, b. p. 69—70°/20 mm. or 160—162°/760 mm., D_4^0 0·994, is a colourless, mobile oil, and furnishes a *semicarbazone*, m. p. 125°, and an *oxime*, m. p. 66°, b. p. 125°/20 mm. The *ethyl* ester, b. p. 76—77°/20 mm., yields a *semicarbazone*, m. p. 115°, and an *oxime*, m. p. 22—23°, b. p. 131—133°/20 mm., which reacts with phenylcarbimide to give a *phenylurethane*, m. p. 123—124°, crystallising in long, brilliant needles. On reduction, the oxime yields *ethyl α-amino-$\beta\beta$-dimethylbutyrate*, $CMe_3\cdot CH(NH_2)\cdot CO_2Et$, b. p. 83°/15 mm., D_4^0 0·952, which with phenylcarbimide yields the corresponding *phenylcarbamide*, m. p. 78°, with benzoyl chloride gives *ethyl ψ-butylhippurate*, m. p. 64°, b. p. 198—200°/15 mm., and also yields a *picrate*, m. p. 134°.

Trimethylpyruvic acid condenses with aniline to form a product which, on distillation, yields $\alpha\alpha$-dimethylpropaldehyde (compare Bouveault, Abstr., 1896, i, 649) and some *$\beta\beta$-dimethylpropylideneaniline*, $CMe_3\cdot CH\colon NPh$, b. p. 101—102°/20 mm., D_4^0 0·941. $\alpha\alpha$-Dimethylbutaldehyde yields an *oxime*, m. p. 41°, b. p. 65°/20 mm., and an *azine*, m. p. 79°. Ethyl trimethylpyruvate combines with anhydrous hydrogen cyanide in presence of trimethylamine, forming the cyanohydrin (Carlinfanti, Abstr., 1899, i, 671), and this, on hydrolysis with sulphuric acid at $-15°$, is converted into the *amide*

of *ethyl ψ-butyltartronate*, $CMe_3 \cdot C(OH)(CO \cdot NH_2) \cdot CO_2Et$, m. p. 60°, b. p. 162—164°/15 mm. With ammonia in alcohol, ethyl trimethylpyruvate forms a *substance*, $C_{12}H_{21}O_2N_3$, m. p. 225°, which is crystalline.

When methyl or ethyl trimethylpyruvate is treated with magnesium methyl iodide or magnesium methyl bromide, α-hydroxy-αββ-trimethylbutyric acid or its ester is formed, with a small amount of the aldehyde corresponding with this acid. Pinacolin combines with hydrogen cyanide to form α-hydroxy-αββ-trimethylbutyronitrile (Carlinfanti, Abstr., 1898, i, 234), m. p. 113°, b. p. 90°/12 mm., and this on treatment with sulphuric acid at 0° is hydrolysed to the *amide*, m. p. 140—141°, b. p. 170°/10 mm. (decomp.), which is converted by boiling with hydrochloric acid into *α-hydroxy-αββ-trimethylbutyric acid*, $CMe_3 \cdot CMe(OH) \cdot CO_2H$, m. p. 141°, b. p. 130°/14 mm. The *methyl* ester, b. p. 65·5°/12 mm., D_4^0 1·002, and the *ethyl* ester, b. p. 74°/12 mm., D_4^0 0·975, are oils, the latter having a camphoraceous odour. The acid condenses with chloral to form a *chloralide*, m. p. 85°, b. p. 126—127°/14 mm.

When methyl hydroxytrimethylbutyrate is treated with magnesium methyl iodide, it yields (1) *α-hydroxy-αββ-trimethylbutaldehyde*, b. p. 82—84°/16 mm., which gives an *oxime*, m. p. 65°, b. p. 126—127°/15 mm., that regenerates the nitrile on treatment with acetic anhydride, and (2) *ββγδ-tetramethylamylene βγ-glycol*, $HO \cdot CMe_2 \cdot CMe(OH) \cdot CMe_3$, m. p. 22°, b. p. 96—98°/16 mm., and this, when boiled with 20% sulphuric acid, furnishes the hexamethylacetone described by Haller and Bauer (Abstr., 1910, i, 219).

α-Hydroxy-ββ-dimethylbutyric acid yields a *chloralide*, m. p. 63°, b. p. 130°/15 mm., and, when heated at 240°, gives αα-dimethylpropaldehyde (see above) and a less volatile material, which, on distillation under reduced pressure, furnishes (1) *trimeric αα-dimethylpropaldehyde*, b. p. 104—105°/18 mm., D_4^0 0·979, and (2) the *dilactide* of *α-hydroxy-ββ-dimethylbutyric acid*, m. p. 84°, b. p. 148°/13 mm., a substance crystallising in brilliant spangles. αα-Dimethylpropaldehyde combines with hydrogen cyanide in presence of pyridine, forming *α-hydroxy-ββ-dimethylbutyronitrile*, b. p. 100°/100 mm., D_4^0 0·911, and this, on hydrolysis by sulphuric acid at 0°, gives the corresponding *amide*, m. p. 135°, which, when boiled with hydrochloric acid, furnishes the corresponding acid; the *methyl* ester of the latter has b. p. 69—70/16 mm., D_4^0 1·044, and the *ethyl* ester has b. p. 79—80°/16 mm. and D_4^0 0·987. The acid, on treatment with phosphorus pentachloride, followed by methyl alcohol, furnishes (1) a *liquid*, $C_9H_{19}O_6P$, b. p. 165—170°/23 mm., D_4^0 1·437, which is neutral to litmus, and possesses an alliaceous odour; (2) dimethyl hydrogen phosphate; (3) methyl hydroxydimethylbutyrate; (4) an *acid*, b. p. 75—90°/22 mm., and (5) a second *acid*, b. p. 150—155°/22 mm. The first substance probably has the constitution

$$PO(OMe)_2 \cdot O \cdot CH(CMe_3) \cdot CO_2Me.$$

Under like conditions with phosphorus pentabromide, a neutral substance, $C_7H_{13}O_2Br$, b. p. 115—125°/23 mm., is formed. Phosphorus tribromide reacts with ethyl hydroxydimethylbutyrate to give two products, *one* having b. p. 85—90°/20 mm., and the *other*,

190—215°/20 mm. With phosphorus tri-iodide the methyl ester yields an *iodo*-compound, having b. p. 102—105°/18 mm., and a *substance*, b. p. 200°/18 mm. (approx.), which contains phosphorus.

T. A. H.

The Photo-chemical Inversion of Maleic Acid. Ludwik Bruner and M. Królikowski (*Bull. Acad. Sci. Cracow*, 1910, 192—208).—As a preliminary step in the investigation of the photochemical transformation of maleic into fumaric acid in presence of a small quantity of bromine, the authors have measured the rates at which the two acids take up bromine with the formation of dibromosuccinic acid. The experiments were made in dilute aqueous solntion at 25° in the dark, the reacting substances being present in equimolar proportions. The values obtained for the velocity constant, on the assumption that the reaction is bimolecular, decrease as the reaction proceeds, and this is found to be due to the increasing acidity of the solution as a consequence of the formation of bromomalic acid and hydrobromic acid by hydrolysis of the dibromosuccinic acid formed in the primary reaction. In support of this view, it is found that the addition of mineral acids diminishes the rate of the reaction, but if these are present in considerable excess, the progress of the reaction is in agreement with the equation for a bimolecular change. Under these conditions it is found that the rate at which bromine is taken up by maleic acid is fifteen times as great as for fumaric acid.

In connexion with the photo-chemical inversion, two methods have been worked out for the quantitative estimation of fumaric and maleic acids in their mixed solutions. These depend respectively on measurements of the electrical conductivity and of the solubility of fumaric acid in the solutions.

The rate of transformation of maleic acid into fumaric in presence of a trace of bromine and in sunlight shows that the reaction is unimolecular. If the light is removed whilst the reaction is in progress, the inversion process ceases, and there appears to be no after effect. The active rays are those at the blue end of the spectrum, the reaction ceasing when a 2 cm. layer of 7·5% potassium dichromate or of 5% bromine solution is interposed.

Between 16° and 32° the velocity of the inversion is practically independent of the temperature. The proportion of maleic acid, which is transformed when the reaction comes to an end, increases with the amount of bromine present in the solution. For small concentrations of bromine, the percentage of fumaric acid in the equilibrium mixture is approximately proportional to the quantity of bromine present.

For a definite amount of bromine the proportion of fumaric acid in the final mixture diminishes as the concentration of the maleic acid increases. If fumaric acid is added to the original solution, the proportion of maleic acid which is inverted diminishes. On the other hand, addition of other acids, such as nitric and sulphuric acids, increases the proportion of the maleic acid which is finally transformed.

H. M. D.

Action of Zinc and Magnesium Organic Compounds on Ortho-formic Ester. M. L. Shdanovitsch (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1279—1297).—When zinc reacts on a mixture of ethyl ortho-formate and ethyl α-bromo*iso*butyrate in the absence of any solvent, the following products are obtained: (1) *Ethyl ββ-diethoxy-αα-dimethylpropionate*, $CH(OEt)_2\cdot CMe_2\cdot CO_2Et$, b. p. 211—212°/748·2 mm., D_{19}^{19} 0·9520, n_{19} 1·41886, which when heated with nitric acid readily yields dimethylmalonic acid, m. p. 184—185·5° (decomp.). (2) Ethyl tetramethylacetoacetate, $CHMe_2\cdot CO\cdot CMe_2\cdot CO_2Et$, which when hydrolysed with hydrochloric acid yields di*iso*propyl ketone, the semicarbazone of which has m. p. 153—154·5° (Blaise gives 150—151°). (3) *Ethyl γ-keto-ααββδδ-hexamethyladipate*,

$$CO_2Et\cdot CMe_2\cdot CMe_2\cdot CO\cdot CMe_2\cdot CO_2Et,$$

b. p. 303—309°/760 mm. (4) An *unsaturated keto*-ester, probably $CH_2{:}CMe\cdot CO\cdot CMe_2\cdot CO_2Et$, which on hydrolysis yields methacrylic acid, $CH_2{:}CMe\cdot CO_2H$, of which the silver salt was analysed. (5) The resinous product obtained after the distillation of the crude product yields, on hydrolysis, a quantity of cubic crystals, possibly tetramethylsuccinic acid. The *silver* salt, $C_{13}H_{19}O_6Ag_3$ or $C_8H_{12}O_4Ag_2$, was analysed; some butaldehydes were also found amongst the products. When magnesium is substituted for zinc, the chief products of the reaction are: (1) ethyl tetramethylacetoacetate; (2) *ethyl β-keto-δδ-diethoxy-ααγγ-tetramethylvalerate*,

$$CH(OEt)_2\cdot CMe_2\cdot CO\cdot CMe_2\cdot CO_2Et,$$

b. p. 160—161°/23 mm., 272—273°/760 mm., a yellow liquid with a pleasant sweet odour; (3) ethyl β-hydroxytetramethylglutarate,

$$CO_2Et\cdot CMe_2\cdot CH(OH)\cdot CMe_2\cdot CO_2Et,$$

which is separated from the acetal with great difficulty. Z. K.

Cholic Acid. II. Martin Schenck (*Zeitsch. physiol. Chem.*, 1910, **69**, 383—389).—Reductodehydrocholic acid (Abstr., 1910, i, 10) is now found to have m. p. 190—192° (not sharp), and is dextrorotatory, $[\alpha]_D = +29°$, when dissolved in alcohol. It appears to be identical with the acid obtained by Hammarsten by reducing dehydrocholic acid with sodium amalgam.

A modified method is given for obtaining cholic acid from ox gall and for preparing some of its known derivatives; for this the original paper must be consulted. An examination of cholanic acid, $C_{24}H_{36}O_7$, showed that six of the oxygen atoms are in three carboxyl groups, while the seventh is in a keto-group. The author has succeeded in preparing an oxime, $C_{24}H_{36}O_6{:}N\cdot OH$, crystallising in plates or needles from acetone, which begins to decompose at 160°, and is completely decomposed at 197°. E. J. R.

Complex Derivatives of Molybdic Acid. Arrigo Mazzucchelli (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 439—445. Compare Abstr., 1910, i, 657, 708).—Determinations of the rotatory power of solutions of tartaric acid and molybdates are complicated by the variations in the acidity and ionisation with the composition of the solution, and it is preferable to examine solutions containing only tartaric and molybdic acids. The addition of other acids to such a solution lowers the

rotatory power, hydrochloric acid having a greater effect than acetic, and the rotatory power tends to a limit when the quantity of hydrochloric acid is increased. The conclusion is drawn that the exaltation observed on adding further quantities of molybdic acid to molybdotartaric acid is specific, and is due to the formation of complexes. Cryoscopic determinations show that the group $C_4H_4O_6,MoO_3$, is largely polymerised in solution. On the other hand, sodium molybdo-oxalate has a normal molecular weight. C. H. D.

Complexes of Permolybdic and Pertungstic Acids with Active Organic Acids. ARRIGO MAZZUCCHELLI and MARIO BORGHI (*Gazzetta*, 1910, **40**, ii, 241—261).—The rotatory power of the *ammonium molybdotartrate*, $(NH_4)_2C_4H_4O_6,MoO_3$, at different concentrations agrees fairly well with those observed by Rosenheim and Itzig (Abstr., 1900, i, 135, 272) for the potassium and sodium salts of this composition, so that it may be considered to produce the same active ion. To solutions of this salt containing in combination 1·646% of tartaric acid (by volume), hydrogen peroxide was added in the quantity required by the ratio $MoO_3 : 2H_2O_2$. The specific rotatory power of the tartaric acid is thereby reduced from $+528°$ to $+203°$. It rises again when the solution is kept, owing to catalytic decomposition of the hydrogen peroxide, and if this decomposition is accelerated by the addition of amyl alcohol (compare Brode, Abstr., 1901, ii, 433) the specific rotatory power reaches its initial value in the course of some hours. The change of specific rotatory power caused by hydrogen peroxide is not due to scission of the molybdotartaric ion into ozomolybdate and tartaric acid, because when more hydrogen peroxide is added, making the ratio $MoO_3 : 3H_2O_2$, no further change in rotatory power occurs. The specific rotatory power in a solution containing hydrogen peroxide in the ratio $MoO_3 : 3H_2O_2$ diminishes on dilution.

The authors have made experiments to ascertain whether complex ozo-salts exist corresponding with the molybdotartrates containing other numbers of molybdenum trioxide groups, the method adopted being to mix hydrogen peroxide with solutions of tartaric acid and of the yellow acid, $MoO_3,2H_2O$ (compare Rosenheim, Abstr., 1906, ii, 762). The rotatory power attains a maximum when the solution contains $C_4H_4O_6,4MoO_3,4H_2O_2$, so that the existence of a complex of this composition is probable, although for other reasons not certain.

Rosenheim has shown (Abstr., 1904, ii, 128) that white molybdic acid, MoO_3,H_2O, differs from the yellow dehydrated acid, $MoO_3,2H_2O$, even in solution. White α-molybdic acid is readily obtained by treating methyl molybdate with water. Its behaviour with tartaric acid and hydrogen peroxide is analogous to that of the yellow acid, but the rotatory powers of solutions of the same composition are different, and the maximum corresponds with the existence of a compound $C_4H_4O_6,5(MoO_3,H_2O_2)$, thus affording a further proof of the difference between the two acids.

Solutions of sodium molybdomalate, obtained by mixing equimolecular quantities of sodium molybdate and malic acid, containing 1 mol. of hydrogen peroxide, rapidly decompose, and the specific rotatory power of the malic acid returns to the value $+151°$ due to the molybdo-

malate. When an excess of hydrogen peroxide is taken, the specific rotation at first is about $-140°$, but eventually it becomes $+151°$. It is considered that the hydrogen peroxide in the undecomposed solution forms the complex $Na_2C_4H_4O_5,MoO_4$.

Similar experiments with solutions of sodium tungstotartrate, $Na_2C_4H_4O_6.WO_2$, indicate the formation of a complete ozotungstotartrate, which contains probably equimolecular quantities of tungsten trioxide and hydrogen peroxide (compare Mazzucchelli and Inghilleri, Abstr., 1908, i, 755). The rotatory power does not alter when the solution is kept, so that the decomposition of the hydrogen peroxide is slower in presence of tungsten trioxide than in the presence of molybdenum trioxide (compare Brode, *loc. cit.*). R. V. S.

Resolution of Pentane-$\beta\beta\delta$-tricarboxylic Acid and of a *s*-Dimethylglutaric Acid into Optically Active Components. ELOF MÖLLER (*Ber.*, 1910, 43, 3250—3251).—Pentane-$\beta\beta\delta$-tricarboxylic acid, $CMe(CO_2H)_2\cdot CH_2\cdot CHMe\cdot CO_2H$, obtained by condensing ethyl α-bromo*iso*butyrate with the sodio-derivative of ethyl *iso*succinate and hydrolysing the resulting ester, separates from water in slender crystals, and has $K = 0{\cdot}220$ at 25°. The *potassium* salt, $C_8H_{11}O_6K$, forms readily soluble prisms, and the *normal* salt, $C_8H_9O_6K_3,H_2O$, transparent, deliquescent crystals. It can be resolved by means of strychnine; the salt of the *d*-acid is sparingly soluble, and crystallises in long, pointed needles, whereas the salt of the *l*-acid forms long, transparent prisms. The *d*-acid has $[\alpha]_D^{20}$ $+16{\cdot}3°$, and the *l*-acid $[\alpha]_D^{20}$ $-15{\cdot}6°$, in aqueous solution. The *d*-acid evolves carbon dioxide at 140°, and yields a dimethylglutaric acid with $[\alpha]_D^{20}$ $+16{\cdot}2°$; the *l*-acid under similar conditions yields a dibasic acid with $[\alpha]_D^{20}$ $-15{\cdot}7°$. The inactive acid evolves carbon dioxide at 135°, and at 140° yields a mixture of the two *s*-dimethylglutaric acids. These can be separated by means of their calcium hydrogen salts, and the acid with m. p. 140—141° can be resolved by means of strychnine into its active constituents. The salt of the *d*-acid crystallises, first, in large prisms, and then the salt of the *l*-acid in small, felted needles.

The *d*-acid has $[\alpha]_D^{20}$ $+41{\cdot}9°$, and the *l*-acid, $[\alpha]_D^{20}$ $-24{\cdot}3°$. The acid melting at 141° is thus the racemic form, and the acid with m. p. 128° the meso-form. J. J. S.

Glucodeconic Acids. L. H. PHILIPPE (*Compt. rend.*, 1910, 151, 986—988).—The preparation of α-glucodeconic acid, $C_{10}H_{20}O_{11}$, from gluconose by Fischer's method is described. The acid could not be isolated in a pure state, since on concentrating its aqueous solutions, crystals were deposited consisting of an hydrated *lactone*,

$$C_{10}H_{18}O_{10},H_2O,$$

m. p. 168° (anhydrous, m. p. 214°), $[\alpha]_D^{20}$ $-37{\cdot}2°$, together with an *anhydride*, $(OH\cdot CH_2\cdot[CH(OH)]_8\cdot CO)_2O$, m. p. 250°. These were separated by taking advantage of the much greater solubility of the former compound. Both substances after hydrolysis yield the same *phenylhydrazide*, crystallising in rectangular lamellæ, m. p. 268°. The acid forms an ill-defined *amide*, $C_{10}H_{21}O_{10}N$, m. p. about 250°. The *sodium*, *barium*, *zinc*, *copper*, *lead*, and *cadmium* salts are sparingly soluble;

the *brucine*, *quinine*, *morphine*, and *strychnine* salts have been prepared. W. O. W.

The Oxidation of Aldehydes in Alkaline Solution. GEORGE W. HEIMROD and PHŒBUS A. LEVENE (*Biochem. Zeitsch.*, 1910, 29, 31—59).—The authors studied the oxidation of various substances in alkaline solution, using principally hydrogen peroxide as the oxidising agent, and, by means of a specially constructed apparatus which is figured, estimated the hydrogen evolved, and also estimated the carbon dioxide and formic acid formed. They confirmed the observations of previous observers that formaldehyde yields on treatment with hydrogen peroxide, hydrogen gas, and assumed that the evolution of this gas is evidence of the formation of formaldehyde as an intermediate product of oxidation when it is obtained from other substances. Ethylene glycol, under the conditions of oxidation chosen, evolved no hydrogen, whereas glycerol did, and the authors give equations to represent what they consider to be the mechanism of oxidation of this substance. They also investigated the oxidation of acetaldehyde, and its possible intermediate oxidation products, glycollaldehyde, glyoxal, glycollic acid, and glyoxylic acid, estimating in each case the carbon dioxide and formic acids formed, and give equations showing the various courses of oxidation possible. As a result of their experiment, they draw the conclusion that acetaldehyde oxidises through the following stages: acetaldehyde (vinyl alcohol) $\longrightarrow$ glycollaldehyde $\longrightarrow$ glyoxal $\longrightarrow$ formic acid $\longrightarrow$ carbon dioxide. There is no evidence of the formation of formaldehyde as an intermediate product. The reaction rates of the oxidation of acetaldehyde under various conditions were also investigated. S. B. S.

Preparation of Aldehyde Diacetates. ALFRED WOHL and RUDOLF MAAG (*Ber.*, 1910, 43, 3291—3295. Compare Mannich and Hâncu, Abstr., 1908, i, 245; Semmler, Abstr., 1909, i, 239, 312, 364, 594; Wohl and Berthold, Abstr., 1910, i, 620; Blanksma, Abstr., 1909, i, 779; Wegscheider and Späth, Abstr., 1910, i, 155).—It is pointed out that the formation of a monoacetate of the type $R\cdot CH\colon CH\cdot OAc$ does not necessarily mean that the aldehyde exists in the tautomeric enolic form, as the monoacetates are formed at high temperatures only, whereas diacetates of the type $R\cdot CH_2\cdot CH(OAc)_2$ are formed at moderate temperatures, and it is highly probable that the monoacetates are formed by the decomposition of diacetates at the high temperature used:

$$R\cdot CH_2\cdot CH(OAc)_2 = R\cdot CH\colon CH\cdot OAc + AcOH.$$

It is shown that Wegscheider's yields can be materially improved if an excess of acetic anhydride is avoided; thus a 90% yield of acetaldehyde diacetate is formed when 1·25 mols. of aldehyde are used for 1 mol. of anhydride, and a 70% yield when equimolecular quantities are taken.

α-Keto-γ-acetoxyvaleric acid, $OAc\cdot CHMe\cdot CH_2\cdot CO\cdot CO_2H$, obtained by heating a mixture of molecular quantities of pyruvic acid, acetaldehyde, and acetic anhydride for five hours at 100° and distilling under reduced

pressure, is a colourless oil, b. p. 100—103°/12 mm. and does not decolorise bromine. Ethylidene diacetate is formed at the same time. A good yield of the latter can be obtained by heating paraldehyde with acetic anhydride and a few drops of concentrated sulphuric acid for an hour at 100°.

Acraldehyde diacetate, 64% yield, is best prepared at the ordinary temperature.

Phenylacetaldehyde diacetate, $CH_2Ph\cdot CH(OAc)_2$, has b.p. 147°/15 mm., and the monoacetate of the enolic form does not appear to be formed. A less volatile fraction, however, yields a small amount of glistening plates, $C_{20}H_{22}O_5$, probably $(CH_2Ph\cdot CH\cdot OAc)_2O$. J. J. S.

The History of Chemical Fermentation Hypotheses. WALTHER LÖB (*Biochem. Zeitsch.*, 1910, 29, 311—315).—A theoretical paper, in which the author, as a result of data obtained from his investigations on the action of the silent discharge on sugar solutions, etc., suggests that one molecule of sugar may first undergo scission into two molecules (glyceraldehyde or dihydroxyacetone), which themselves can undergo further scission into glycollaldehyde and formaldehyde, and, finally, into formaldehyde only. Ethyl alcohol can be formed by reaction between glycollaldehyde and formaldehyde, carbon dioxide being formed at the same time. Equations are given to explain the phenomena. S. B. S.

Mutarotation and Electrical Conductivity of Carbohydrates. I. Dextrose. PAUL RABE and CHARLES ROY (*Ber.*, 1910, 43, 2964—2971).—*N*/10-Solutions of dextrose show no change in conductivity after twenty-four hours at 20°, during which the rotation falls from $[\alpha]_D^{20}$ +97·5° to +50°. No change was observed even with the most delicate instruments after five months' further keeping.

E. F. A.

β-Dextrose. ROBERT BEHREND (*Annalen*, 1910, 377, 220—223).—The separation of β-dextrose by cooling a hot solution of α-dextrose in pyridine (Abstr., 1907, i, 481) can only be explained if the β-dextrose crystallises with pyridine. If the β-dextrose separates as such, it is possible by selecting two suitable solvents at the same temperature and pressure to create a system in which perpetual motion must occur. It is shown that the β-dextrose does separate in crystals, which rapidly weather and lose pyridine in amount corresponding approximately with 1 molecule of pyridine of crystallisation.

The author arrives at the same result as Dimroth (compare this vol., ii, 31), namely, that the same substance must always separate from solutions, at the same temperature and pressure, of two mutually interconvertible isomerides in any solvent, provided that by-products are not formed. C. S.

Hexoses from *d*-Ribose. PHŒBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1910, 43, 3141—3147).—The four unknown aldohexoses are theoretically to be derived from the isomeric riboses, but the lack of these pentoses, has hitherto prevented the synthesis of the hexoses.

Nucleic acids now afford a relatively simple means of obtaining *d*-ribose in some quantity, and by the application of the cyanohydrin synthesis, d-*allose* and d-*altrose* have been obtained. They have the annexed configuration.

$$\begin{array}{cc}
\begin{array}{c} \mathrm{CHO} \\ | \\ \mathrm{H\cdot C\cdot OH} \\ | \\ \mathrm{H\cdot C\cdot OH} \\ | \\ \mathrm{H\cdot C\cdot OH} \\ | \\ \mathrm{H\cdot C\cdot OH} \\ | \\ \mathrm{CH_2\cdot OH} \end{array} &
\begin{array}{c} \mathrm{CHO} \\ | \\ \mathrm{HO\cdot C\cdot H} \\ | \\ \mathrm{H\cdot C\cdot OH} \\ | \\ \mathrm{H\cdot C\cdot OH} \\ | \\ \mathrm{H\cdot C\cdot OH} \\ | \\ \mathrm{CH_2\cdot OH} \end{array} \\
d\text{-Allose.} & d\text{-Altrose.}
\end{array}$$

Both are syrups insoluble in alcohol, and have not been obtained free from impurities. They yield the same phenylosazone, and *d*-altronic acid yields talomucic acid on oxidation.

Calcium d-*altronate* is obtained by the addition of hydrogen cyanide to *d*-ribose and hydrolysis of the nitrile formed with barium hydroxide. The solution is rendered slightly acid, and treated in turn with lead carbonate, hydrogen sulphide, and calcium carbonate. It crystallises in thick crusts of cauliflower-like aggregates of needles. The free *acid* is a colourless syrup; the specific rotatory power increases in solution, $[\alpha]_D^{30}$ $+35\cdot14°$.

On reduction, *d*-altrose is obtained as a syrup. The *phenylbenzylhydrazone* crystallises in well formed, yellow, lustrous plates, which sinter at 145°, m. p. 148—150° (corr.). d-*Altrosephenylosazone*, crystallises in long, thin, matted needles or stellate aggregates of platelets, which sinter at 175°, m. p. 183—185° (corr.). It is lævorotatory in pyridine solution.

The mother liquors from the calcium altronate contain calcium allonate. d-*Allonolactone*, $C_6H_{10}O_6$, forms long, colourless prisms, which sinter at 97° and are completely melted to a clear liquid at 120°, and have $[\alpha]_D^{20}$ $-6\cdot79°$ ($\pm 0\cdot2°$). d-*Allose*-p-*bromophenylhydrazone* crystallises in lustrous plates, which sinter at 143°, m. p. 145—147° (corr.), $[\alpha]_D^{30}$ $-6\cdot7°$. E. F. A.

Constitution of Vicianose and of Vicianin. Gabriel Bertrand and Gustave Weisweiller (*Compt. rend.*, 1910, **151**, 884—886. Compare Abstr., 1906, i, 68; 1908, i, 817; Abstr., 1910, i, 156).—The new sugar vicianose, prepared from vicianin, a glucoside occurring in the vetch, has been oxidised by bromine water in presence of calcium carbonate. A calcium vicianobionate was thus obtained, which on hydrolysis gave calcium gluconate and *l*-arabinose. Vicianose, therefore, appears to have the constitution:

$$\mathrm{O}\!\!<\!\!\begin{array}{l}\mathrm{CH\cdot[CH\cdot OH]_2\cdot CH_2\cdot OH} \\ |\\ \mathrm{CH\cdot O\cdot CH_2\cdot[CH\cdot OH]_2\cdot CHO}\end{array},$$

whilst the glucoside is represented as:

$$\mathrm{O}\!\!<\!\!\begin{array}{l}\mathrm{CH\cdot[CH\cdot OH]_2\cdot CH_2\cdot OH} \\ | \\ \mathrm{CH\cdot O\cdot CH_2\cdot[CH\cdot OH]_3{-}\overset{\quad O \quad}{CH{-}CH}\cdot O\cdot CHPh\cdot CN}\end{array}.$$

The other properties of the substances described previously are in agreement with these representations. W. O. W.

The Degradation of the Sugar Group. Adolf Jolles (*Biochem. Zeitsch.*, 1910, **29**, 152—201).—It is shown that the majority of the sugars undergo chemical change at 37° when treated with *N*/100-

alkali hydroxide, the optical rotation of the solution decreasing and the acidity increasing. The latter change continues after the former change has ceased. In certain cases, as, for example, that of sucrose, the change is small. The rate of acid formation is increased by the addition of hydrogen peroxide and silver oxide, although the addition of oxidising reagents does not affect the rate of change in optical activity. Ferments exert but slight influence. If sugars be kept in alkaline medium, the estimation by polariscope becomes, owing to the above-mentioned changes, untrustworthy, although they do not affect the reducing powers. Formic acid and, in case of certain sugars, acetaldehyde were detected as reaction products. Polyhydroxy-acids were not found. The author gives a large number of data showing the rate of the changes in various sugars. S. B. S.

Mutarotation of Maltose. GERHARD SCHLIEPHACKE (*Annalen*, 1910, **377**, 164—188).—The theory that the mutarotation of a sugar in solution is due to the equilibrium of the two stereoisomeric lactone forms of the sugar with one another, and probably also with the aldehydic form, is supported by the relations which have been shown to exist between dextroses of different rotatory powers and their penta-acetates (Behrend and Roth, Abstr., 1904, i, 716), and between galactoses of different rotatory powers and their penta-acetates (Heikel, Abstr., 1905, i, 173). The author has now examined a biose, maltose, with regard to its mutarotation and its acetates. Dissolved in pyridine, the sugar has $[\alpha]_D^{20}$ +97·7° forty minutes after solution, and 122·2° after fourteen days; after being warmed to 50° for ten minutes, the solution attains a constant rotatory power, $[\alpha]_D^{20}$ +123·5°. After being boiled for three minutes and then cooled, the solution attains its maximum rotation, having $[\alpha]_D^{20}$ +128·8°, which falls to 124·0° after one hundred and thirty-two hours.

Ordinary maltose belongs probably to the β-series, since it yields, when acetylated under suitable conditions, chiefly the only known crystalline acetate, Herzfeld's maltose octa-acetate, m. p. 155—156°, which belongs to the β-series, having been converted into β-methylglucoside by Königs and Knorr. When solid maltose in the presence of pyridine at 0° is treated with acetic anhydride, it yields a crude acetate, from which 73·9% of crystallised β-octa-acetate has been obtained together with a syrup which has the composition of an octa-acetate and $[\alpha]_D$ +101·3° in benzene. When a solution of maltose in pyridine, of constant rotation, is acetylated at 0°, 36·1% of the crystallised β-octa-acetate and a syrup having $[\alpha]_D$ +107·4° in benzene are obtained. Finally, when the pyridine solution of maximum rotation obtained by boiling is acetylated at 0°, only 18·8% of the crystallised β-octa-acetate is obtained, together with a syrup having $[\alpha]_D$ +110·6°. These results indicate that the solution of maltose in pyridine contains ordinary β-maltose (which yields the β-octa-acetate) in equilibrium with another or, more probably, two other forms of maltose (which yield the syrup). The rotation of the unknown α-maltose octa-acetate, calculated by Hudson's theory (Abstr., 1909, i, 135), corresponds with $[\alpha]_D$ +131·88° in benzene and +117·51° in chloroform; the values are given with reserve, since it is as yet

uncertain whether Hudson's theory is applicable to the acetates of the sugars.

When maltose is acetylated in pyridine there is produced, together with the octa-acetates, about 6% of a *hexa-acetate,* which is an amorphous powder having $[\alpha]_D + 133\cdot96°$ in benzene and $139\cdot96°$ in chloroform; it separates together with the β-octa-acetate from alcoholic solutions, and is separated therefrom mechanically.

By treating β-maltose octa-acetate with liquid hydrogen chloride, Fischer and Armstrong obtained a hepta-acetylchloromaltose having m. p. 66—68° and $[\alpha]_D^{20} + 176\cdot0—177\cdot1°$ in benzene. By treating maltose with acetic anhydride and hydrogen chloride, Foerg obtained a hepta-acetylchloromaltose having m. p. 118—120° and $[\alpha]_D$ $-159°$ in chloroform. The author hoped to get α-maltose octa-acetate from the latter, but by treatment with glacial acetic acid and anhydrous sodium acetate on the water-bath, it yielded the β-isomeride. The author confirms Foerg's m. p. for the substance, but finds that it has $[\alpha]_D + 158\cdot68°$ in chloroform and $175\cdot66°$ in benzene, the latter value being almost identical with the corresponding value of Fischer and Armstrong's compound. The relation between these two substances, having the same rotatory power but different m. p.'s, has not yet been ascertained; both give the same β-hepta-acetylmethylmaltoside by treatment with methyl alcohol and silver carbonate. C. S.

Carbohydrates Occurring in Seeds. Ernst Schulze and Urs Pfenninger (*Zeitsch. physiol. Chem.*, 1910, **69**, 366—382).—A large number of plant seeds contain soluble carbohydrates that give mucic acid on oxidation with nitric acid, and therefore yield galactose on hydrolysis. Raffinose is known to occur in cotton seed, in the embryos of wheat, and of certain leguminous plants; the authors now describe another carbohydrate, *lupeose,* which has not yet been crystallised, but is, they believe, a single substance and not a mixture.

Lupeose has been extracted from seeds of *Lupinus luteus* and *Lupinus angustifolius* by extraction either with hot dilute alcohol or with water; it is then obtained from this solution by precipitation with alcohol. It forms a white powder, readily soluble in water, and does not reduce Fehling's solution until it has been heated with acids. It is dextrorotatory; the different preparations in 4 or 5% solution have given $[\alpha]_D = +138°$ to $+144°$, the differences no doubt arising from the presence of impurities. Oxidation with nitric acid gives rise to 38—40% of mucic acid; presumably, therefore, galactose constitutes half of the products of hydrolysis. Lævulose is also formed on hydrolysis, and there appears to be a third sugar. For this and other reasons lupeose is considered to be more complex than a disaccharide. In several ways lupeose resembles stachyose, but the differences are sufficient to justify the conclusion that the two are distinct. E. J. R.

Mercerised Cellulose. Oswald Miller (*Ber.*, 1910, **43**, 3430—3435. Compare Vieweg, Abstr., 1907, i, 893; Schwalbe, *ibid.*, 1909, i, 136, 366).—If cellulose is dried for six hours at 95° both before and after

treatment with concentrated sodium hydroxide solution at 10°, there is practically no alteration in weight. The loss in weight of the mercerised product when dried at 95° is the same as when the drying takes place at 22—23° over calcium chloride. Analyses also show that the mercerised and not mercerised compounds have the same percentage composition. That the compounds, however, are not identical has been proved by Wichelhaus and Vieweg (Abstr., 1907, i, 186) by an examination of the products of nitration, and is confirmed by the fact that the amount of water adsorbed by mercerised cellulose is much greater than by ordinary cellulose. The degree of mercerisation can be determined especially by dyeing with rosaniline base; with substantive dyes of the type of geranin-G and chrysophenin an increase in the depth of colour is observed only after the cellulose has been treated with 9% sodium hydroxide solution, and then the colour increases with the concentration of the alkali up to, and probably beyond, 25%. J. J. S.

The Reaction between Humin and Potassium Hypobromite. ARTUR KONSCHEGG (*Zeitsch. physiol. Chem.*, 1910, **69**, 390—394).—The humin was obtained from dextrose by heating 250 grams for twelve hours with 1 litre of 24% hydrochloric acid; the brown flocks produced were then treated with aqueous potassium hydroxide to dissolve out humic acid. The residual humin forms a viscid, mucilaginous mass, that can only with difficulty be separated by filtration from the alkaline solution of humic acid. When dried at 100° it forms a glassy, brittle mass, that breaks down to a powder much darker than humic acid. It is insoluble in water, acids, alkalis, alcohol, or ether.

When, however, humin is suspended in potassium hydroxide and a little bromine added, it passes into solution. After a time, white crystals of tetrabromomethane separate. Humic acid behaves in the same way.

The author finds that humic acid dissolves in water to form a colloidal solution. If the precipitate obtained by adding hydrochloric acid to the alkaline solution of humic acid is washed with water, the filtrate soon begins to be coloured. The dark liquid on evaporation leaves a black, caseous residue soluble both in water and alcohol.

E. J. R.

Chloro-salts of Osmium. ALEXANDER GUTBIER [with K. MAISCH] (*Ber.*, 1910, **43**, 3234—3239).—The substituted ammonium osmichlorides described were prepared by the interaction of the respective substituted ammonium chlorides with sodium osmichloride (Abstr., 1910, ii, 45), than which they are much less soluble; they are all anhydrous and stable in the air. In aqueous solution they undergo decomposition, but in hydrochloric acid solution they are stable. In some cases they are readily soluble in alcohol.

Methylammonium osmichloride, $(NH_3Me)_2OsCl_6$, reddish-brown, anisotropic crystals. *Dimethylammonium osmichloride*,

$$(NH_2Me_2)_2OsCl_6,$$

yellowish-red, rhombic prisms, which are pleochroic. *Trimethyl-*

ammonium osmichloride, $(NHMe_3)_2OsCl_6$, light yellowish-red, regular crystals. *Ethylammonium osmichloride*, $(NH_3Et)_2OsCl_6$, scarlet-red, pleochroic leaflets. *Diethylammonium osmichloride*, $(NH_2Et_2)_2OsCl_6$, yellowish-red, monoclinic crystals. *Triethylammonium osmichloride*, $(NHEt_3)_2OsCl_6$, reddish-yellow, monoclinic needles. n-*Propylammonium osmichloride*, $(NH_3Pr^{\alpha})_2OsCl_6$, dark brownish-red, monoclinic crystals. iso*Propylammonium osmichloride*, $(NH_3Pr^{\beta})_2OsCl_6$, brownish-red, pleochroic crystals. *Dipropylammonium osmichloride*, $(NH_2Pr_2)_2OsCl_6$, reddish-yellow, monoclinic prisms. n-*Butylammonium osmichloride*, $(NH_3{\cdot}C_4H_9)_2OsCl_6$. brownish-red, monoclinic crystals. iso*Butylammonium osmichloride*, $(NH_3{\cdot}C_4H_9)_2OsCl_6$, dark brownish-red, monoclinic or rhombic crystals. *Ethylenediammonium osmichloride*, $C_2H_{10}N_2OsCl_6$, dark brown, monoclinic crystals. *Propylenediammonium osmichloride*, $C_3H_{12}N_2OsCl_6$, dark brownish-red, monoclinic crystals.

T. S. P.

Nitrilo-trimethylnitroaminomethylene. ANTOINE P. N. FRANCHIMONT (*Rec. trav. chim.*, 1910, [ii], **14**, 355—367.* Compare Abstr., 1910, i, 616, 617; Eschweiler, Abstr., 1894, i, 267).—An investigation (1) of the conditions under which hexamethylenetetra-amine and methylnitroamine react to form nitrilo-trimethylnitroamino-methane, $N(CH_2{\cdot}NMe{\cdot}NO_2)_3$, and (2) of the constitution of the latter. This substance is formed in small quantity when hexamethylenetetra-amine is mixed in aqueous solution with methylnitroamine and boiled for some days, but a better yield is obtained when water is replaced by a solution of formaldehyde, and a quantitative yield when the decomposition products of hexamethylenetetra-amine, namely, formaldehyde and ammonia, are mixed with methylnitroamine and slightly warmed.

Nitrilo-trimethylnitroaminomethane, m. p. 116°, crystallises in colourless, transparent prisms, and gives the nitroamine reaction with zinc and α-naphthylamine. When boiled with alkalis, it decomposes in accordance with the equation $N(CH_2{\cdot}NMe{\cdot}NO_2)_3 + 3H_2O = NH_3 + 3H{\cdot}CHO + 3NHMe{\cdot}NO_2$, whilst with acids the reaction takes place as follows: $N(CH_2{\cdot}NMe{\cdot}NO_2)_3 + 3H_2O = NH_3 + 3H{\cdot}CHO + 3N_2O + 3CH_3OH$. In the former case some of the ammonia combines with the formaldehyde, and the reaction cannot be followed quantitatively, but in the second case ammonia, formaldehyde, and nitrous oxide can be estimated, and the results of these estimations serve to establish the constitution of the substance. When dissolved in chloroform and treated with hydrogen chloride, a crystalline *hydrochloride*,

$$NO_2{\cdot}NMe{\cdot}CH_2{\cdot}NH_2,HCl,$$

is formed, which, on evaporation of its aqueous solution, evolves hydrogen chloride and forms a mixture of ammonium chloride, and a soluble substance giving the nitroamine reaction. T. A. H.

Synthesis of γ-Amino-α-hydroxybutyric Acid and its Trimethyl Derivative. EMIL FISCHER and ALBERT GÖDDERTZ (*Ber.*, 1910, **43**, 3272—3280. Compare Fischer and Zemplén, Abstr., 1910, i, 100).—*γ-Phthalimino-α-hydroxybutyric acid*,

$$C_6H_4(CO)_2{:}N{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H,$$

can be obtained by boiling the corresponding α-bromo-acid (Gabriel

* and *Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 527—530.

and Colman, Abstr., 1908, i, 274) with water and calcium or barium carbonate for about fifteen minutes. The *calcium* salt,

$$Ca(C_{12}H_{10}O_5N_2)_2,6H_2O,$$

crystallises from water at 0° in colourless crusts of minute prisms. The *barium* salt also crystallises with $6H_2O$, and when treated with a slight excess of dilute sulphuric acid yields the free acid, which crystallises from hot water in long, colourless needles, containing $1H_2O$, and melting at about 100°; when anhydrous it has m. p. 144—145° (corr.). It has a feebly acidic, but strongly astringent, taste. When hydrolysed with concentrated hydrochloric acid in a platinum flask, it yields *γ-amino-α-hydroxybutyric acid hydrochloride* and phthalic acid. The *hydrochloride*, $C_4H_9O_3N,HCl$, crystallises from a mixture of alcohol and ethyl acetate in colourless needles. The *platinichloride* crystallises from warm alcohol in orange-coloured plates; the *acid*, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$, crystallises from dilute alcohol, and has m. p. 191—192° (corr.). It has no characteristic taste, is not precipitated by phosphotungstic acid, and when heated at 210° for five minutes yields 3-*hydroxypyrrolidone*, $OH{\cdot}CH{<}\begin{matrix}CH_2{\cdot}CH_2\\ CO-NH\end{matrix}$, which crystallises from ethyl acetate at 0° in thin plates, m. p. 85° (corr.). It has a sweet taste, yields a crystalline mercury derivative, and is partly hydrolysed to the amino-acid when boiled with 25% hydrochloric acid. The pyrrolidone is also formed when an alcoholic solution of the amino-acid is saturated with hydrogen chloride.

α-Hydroxy-γ-trimethylaminobutyric acid is formed when the amino-acid is exhaustively methylated. The *sulphate* is readily soluble in water; the *aurichloride*, $C_7H_{15}O_3N,HAuCl_4$, crystallises in yellow needles, m. p. 175—176° (corr.) after sintering at 162°. The *hydrochloride* and *platinichloride* are syrups which crystallise slowly. The latter crystallises in long, slender needles, m. p. 216° (decomp.). The methyl derivative is probably identical with *dl*-carnitine. J. J. S.

Preparation of Creatinine from Urine. OTTO FOLIN and FREDERICK C. BLANCK. **Preparation of Creatinine from Creatine.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1910, 8, 395—397, 399—400).—Details are given of the picric acid procedure in the separation of creatinine from urine. Creatine may be converted into creatinine without the use of any solvent or acid. The water of crystallisation of creatine is sufficient. If creatine is placed in a closed bottle and heat applied until a pressure of 4·5 kilos. per square centimetre is reached, and this is kept up for three hours, the contents contain crystalline creatinine. W. D. H.

Creatinine. ERNST SCHMIDT (*Arch. Pharm.*, 1910, **248**, 568—578).—Mainly an introduction to the two following papers, the object of which is the confirmation of Pommerehne and Toppelius' statement that the creatinines from flesh, from urine, or synthetically produced, are all identical (Abstr., 1897, i, 128), not different as claimed by Johnson (Abstr., 1889, 165).

Neubauer's statement (*Annalen*, 1861, **119**, 49) that creatinine when alkylated behaves as a tertiary base has been denied by

Korndörfer (Abstr., 1904, i, 768), whose results are now confirmed by the fact that creatinine by methylation yields first methylcreatinine, $NMe<\substack{CH_2\cdot CO\\C(:NH)-}>NMe$, and then dimethylcreatinine,

$$NMe<\substack{CH_2-CO\\C(:NMe)}>NMe;$$

the latter then behaves as a tertiary base. C. S.

Methyl-, Dimethyl-, and Trimethyl-creatinines. Gerhard Kunze (*Arch. Pharm.*, 1910, **248**, 578—593).—The methylation of creatinines produced synthetically or from flesh yields methylcreatinine hydriodides, which are identical, and from which identical hydrochlorides, aurichlorides, and platinichlorides are obtained. All these compounds are identical with the corresponding substances obtained by Korndörfer (Abstr., 1905, i, 152) from creatinine prepared from urine.

The base liberated from the methylcreatinine hydriodide by potassium carbonate, lead oxide, or silver oxide is hydrolysed by boiling baryta, yielding carbon dioxide, ammonia, methylamine, and sarcosine, and is oxidised by alkaline 5% potassium permanganate at 50—60° to oxalic acid and Schenck's *s*-dimethylguanidine (Abstr., 1910, i, 99); consequently, the methylcreatinine has the constitution $NH:C<\substack{NMe\cdot CH_2\\NMe\cdot CO}$. By further methylation at 50—70°, it yields dimethylcreatinine hydriodide, m. p. 179—180°; *aurichloride*, m. p. 128—129°; platinichloride, m. p. 177—179° (not 169—170°), the base in which has the constitution $NMe:C<\substack{NMe\cdot CH_2\\NMe\cdot CO}$, since it is oxidised by alkaline potassium permanganate to oxalic acid and Schenck's trimethylguanidine (*loc. cit.*). C. S.

Ethylcreatinine. Carl Henzerling (*Arch. Pharm.*, 1910, **248**, 594—608).—The work is very similar to that of Kunze (preceding abstract), and proves that creatinines obtained from different sources are identical. When alkylated by ethyl iodide, creatinine behaves like a secondary base, yielding *ethylcreatinine hydriodide*,

$$C_6H_{11}ON_3,HI,$$

m. p. 217—219° (from which are formed an *aurichloride* and a *platinichloride*, m. p. 197—211°, monoclinic plates, $a:b:c = 0.8685:1:0.7385$, $\beta = 86°24.5'$), and also creatinine hydriodide, m. p. 195°, as a by-product. The ethylcreatinine hydriodide cannot be an ethiodide, as stated by Neubauer, because the chloride prepared from it is decomposed by potassium carbonate, yielding ethylcreatinine, which has not been obtained crystalline. It is oxidised by alkaline potassium permanganate to oxalic acid and methylethylguanidine (*platinichloride*, m. p. 179—181°), and is hydrolysed by boiling barium hydroxide, yielding carbon dioxide, ammonia, ethylamine, and sarcosine. By treatment with ethyl iodide at 100°, ethylcreatinine yields chiefly ethylcreatinine hydriodide, small quantities of ethylamine and diethylcreatinine (*platinichloride*, m. p. 201—202°) also being formed.

When ethylcreatinine is treated with methyl iodide, the chief product is again ethylcreatinine hydriodide, methylamine and a small amount of methylethylcreatinine (*platinichloride*, m. p. 181—182°) also being formed. C. S.

Propiolic Compounds. Cyanoacetylene, C_3HN. CHARLES MOUREU and J. CHARLES BONGRAND (*Compt. rend.*, 1910, **151**, 946—948. Compare Abstr., 1910, i, 159).—*Propiolamide*,

$$CH⋮C·CO·NH_2,$$

has been obtained by the action of aqueous ammonia at 0° on methyl propiolate. It occurs in lamellæ, m. p. 61—62°; the aqueous solution forms a white precipitate with silver nitrate, and a yellow one with ammoniacal cuprous chloride. When distilled with phosphoric oxide in an atmosphere of carbon dioxide under diminished pressure, cyanoacetylene, CH⋮C·CN, is obtained as a colourless, mobile liquid, b. p. 42·5°/760 mm., D_4^{17} 0·8159, solidifying to crystals, m. p. 5°. The compound is inflammable, and becomes brown on keeping, even in absence of light and air. The vapour is intensely irritating. With silver nitrate, it forms a white explosive substance, whilst the compound obtained by the action of ammoniacal cuprous chloride is green and deflagrates on heating. The molecular refractions for the *D*-sodium line and for the α-, β-, and γ-hydrogen lines have been determined at 17°: M_D 14·7207; $M_\gamma - M_\alpha$ 0·563. Owing to the presence of the acetylenic linking, the refraction and dispersion are higher than the calculated values.

The action of potassium ferricyanide on cyanoacetylene gives rise to a product, which, when sublimed in an atmosphere of carbon dioxide, yields colourless needles, m. p. 64°. This substance has an irritating odour, and the author believes it to be a new carbon subnitride, C_6N_2. W. O. W.

Catalytic Action. IV. Comparison of the Action of Various Catalytic Agents. II. Acetylation of Carbamide. JACOB BÖESEKEN [with Mlle. J. LANGEZAAL] (*Rec. trav. chim.*, 1910, **29**, 330—339. Compare Abstr., 1910, i, 152).—Geuther first effected the acetylation of carbamide, and showed the formation of only a small amount of cyanuric acid, thus differing from the behaviour of the symmetrical di-substituted products of carbamide. The authors show that the difference in behaviour of carbamide and its derivatives is quantitative rather than qualitative.

Various catalytic agents were used in the acetylation, and the results obtained, showing their relative influence and the amounts of acetylcarbamide and cyanuric acid formed, are tabulated in the original.

Various salts of cyanuric acid were made to try and effect its estimation, and the *strontium* salt is described. It was found more convenient to estimate the acid by titration with dilute potassium hydroxide, the acetylcarbamide not being affected.

It was found that on prolonged heating with the catalytic agents, acetylcarbamide is partly decomposed, the percentage of cyanuric acid present increasing. N. C.

Nitrogen and Sulphur Derivatives of Carbon Disulphide. XVII. Tetra-alkylthiocarbamides and Tetra-alkyl*iso*thiocarbamides. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1910, [iv], 7, 988—993).—Compounds of these two types have been prepared previously, but have not been described in detail, and in this paper an account is given of their preparation, properties, and chief derivatives.

The tetra-alkylthiocarbamides are best obtained by Billeter's method, which consists in treating the appropriate secondary amine in benzene or toluene with thiocarbonyl chloride. The tetramethyl compound may be obtained from von Braun and Stechele's tetramethylthiouram sulphide (Abstr., 1903, i, 618) by the action at 100° of dimethylamine dissolved in benzene, thus: $S(CS\cdot NMe_2)_2 + 2NMe_2 = NMe_2\cdot CS\cdot NMe_2 + NMe_2\cdot CS\cdot S\cdot NH_2Me_2$, dimethylamine dimethyldithiocarbamate being also formed. The same two substances result from the action of dimethylamine on dimethylthiouram disulphide: a method analogous with that used by Fromm (Abstr., 1909, i, 506).

The tetra-alkyl*iso*thiocarbamides are obtained by the action of the necessary alkyl iodide on the trialkylthiocarbamides.

The two series of compounds differ considerably in properties. The tetra-alkylthiocarbamides are usually of higher specific gravity and boiling point than their isomerides, and are not basic, whilst their isomerides are markedly basic up to the tetrapropyl compound, which on titration in presence of the usual indicators appears to be saturated before one equivalent of acid has been added. The members of both groups form additive compounds with one mol. of methyl iodide.

Tetramethylthiocarbamide, $S:C(NMe_2)_2$, m. p. 78°, b. p. 245°, is readily soluble in warm, but less so in cold, water (compare Billeter, Abstr., 1910, i, 544). The *methiodide*, $SMeI:C(NMe_2)_2$ or

$$SMe\cdot CI(NMe_2)_2,H_2O,$$

crystallises from alcohol in colourless prisms. On treatment with silver nitrate followed by ammonia, it yields silver methylmercaptide. *Tetraethylthiocarbamide*, b. p. 130°/12 mm., 264—266°/760 mm., D_4^0 0·9804, D_4^{18} 0·9662, is an oily liquid of pleasant odour. *Tetrapropylthiocarbamide*, b. p. 165°/12 mm., or about 305°/760 mm., D_4^0 0·9430, D_4^{19} 0·9300, is a viscid, almost inodorous liquid.

*Tetramethyl*iso*thiocarbamide*, $NMe:C(SMe)\cdot NMe_2$, b. p. 176°, D_4^0 1·0194, D_4^{16} 1·0061, is a colourless liquid of strong odour. The *picrate*, m. p. 99·5°, crystallises in yellow needles. Tetraethyl*iso*thiocarbamide has b. p. 216°, D_4^0 0·9426, D_4^{21} 0·9252 (Grodzky, Abstr., 1882, 823). *Tetrapropyl*iso*thiocarbamide*, b. p. 154°/15 mm., 270°/760 mm. (decomp.), D_4^0 0·9179, D_4^{21} 0·9014, is a colourless, oily liquid of slight odour. It was prepared by the general method from *tripropylthiocarbamide*, m. p. 33°, which crystallises in colourless needles, and was obtained by the union of dipropylamine with propylthiocarbimide. T. A. H.

Formation of Fulminic Acid from Alcohol. HEINRICH WIELAND (*Ber.*, 1910, 43, 3362—3364).—Polemical against Wöhler (Abstr., 1910, i, 231). The following details for the preparation of mercury fulminate from oximinoacetic acid are given. 1·5 Grams of oximinoacetic acid are added to a solution of 1 gram of mercuric

nitrate in 3 c.c. of nitric acid (D = 1·34) and 2 c.c. of water. If the reaction is allowed to go on of its own accord, without cooling, 0·1—0·2 gram of mercury fulminate is obtained, whereas when the reaction is moderated no fulminate is formed. Silver fulminate is obtained in a similar manner. T. S. P.

Chloralurethane. II. OTTO DIELS and ARMENAK GUKASSIANZ (*Ber.*, 1910, **43**, 3314—3320. Compare Abstr., 1909, i, 885).—The constitution, $CCl_2:C(CN)\cdot NH\cdot CO_2Et$, of the nitrile obtained by boiling the acetyl derivative of chloralurethane with aqueous potassium cyanide has been proved by the behaviour of the substance towards ozone and towards nitric acid. The former converts it into carbonyl chloride and a substance (probably $CN\cdot CO\cdot NH\cdot CO_2Et$) which yields oxalic acid by hydrolysis. Warm concentrated nitric acid converts the nitrile into dichlorodinitromethane and oxalic acid.

The action of ethylamine, aniline, piperidine, and sodium ethoxide on the nitrile also supports the constitution. An ethereal solution of the nitrile and ethylamine at 0° yield the *substance*,

$$C(NHEt)_2:C(CN)\cdot NH\cdot CO_2Et,$$

m. p. 104° (corr.), flat plates. The nitrile and aniline, after being heated on the water-bath for one and a-half hours, yield the *substance*, $C(NHPh)_2:C(CN)\cdot NH\cdot CO_2Et$, m. p. 166—167° (corr.). The nitrile and piperidine in ether yield a corresponding substance which, however, cannot be isolated, but is converted by concentrated hydrochloric acid into the *piperidide*, $C_5NH_{10}\cdot CO\cdot C(CN)\cdot NH\cdot CO_2Et$, m. p. 131·5—132·5° (corr.). The nitrile is converted by alcoholic sodium methoxide or sodium ethoxide into the *ortho*-esters,

$$C(OMe)_3\cdot CH(CN)\cdot NH\cdot CO_2Et,$$

m. p. 86—87° (corr.), and $C(OEt)_3\cdot CH(CN)\cdot NH\cdot CO_2Et$, m. p. 56°; when the former is boiled with glacial acetic acid it is converted into *methyl cyanocarbethoxyglycine*, $CO_2Me\cdot CH(CN)\cdot NH\cdot CO_2Et$, m. p. 130·5° (corr), which is easily soluble in alkalis. C. S.

Synthetical Experiments in the Cincholeupone Series. ALFRED WOHL and RUDOLF MAAG (*Ber.*, 1910, **43**, 3280—3291).—Attempts have been made to synthesise cincholeupone derivatives, but, so far, without success. A dimethylpiperidine has been prepared by the following method:

By the addition of ethyl sodiocyanoacetate to the condensation product of aldehyde and acetone, ethyl α-cyano-γ-acetyl-β-methyl butyrate, $CO_2Et\cdot CH(CN)\cdot CHMe\cdot CH_2Ac$, is formed, and when this is hydrolysed and reduced, 2 : 4-dimethylpiperidine is formed.

A fairly good yield of ethylideneacetone (Claisen, Abstr., 1893, i, 8) is obtained by saturating a well cooled mixture of paraldehyde and acetone with dry hydrogen chloride and leaving for two days at 0°. The product obtained by distillation contains appreciable amounts of chlorine, but can be obtained pure by distilling twice over diethylaniline. An impure product, b. p. 120—130°, was used for the condensation with ethyl sodiocyanoacetate. The condensation product, $C_{10}H_{15}O_3N$, has b. p. 155—168°/14 mm., and when hydrolysed with 5*N*-sodium hydroxide solution and distilled, gives a 50% yield

of *δ-keto-β-methylvaleronitrile*, $COMe\cdot CH_2\cdot CHMe\cdot CH_2\cdot CN$, b. p. 105°/11 mm.

The *amide*, $COMe\cdot CH_2\cdot CHMe\cdot CH(CN)\cdot CO\cdot NH_2$, obtained by shaking the cyano-ester with ammonium hydroxide solution, crystallises from alcohol or water, and has m. p. 134°.

The nitrile forms a definite compound with hydrogen chloride, $2C_7H_{11}ON,HCl$, in the form of colourless crystals. The nitrile is not affected by zinc dust and acetic acid, zinc dust and ammonia, sodium amalgam and dilute alcohol, but is reduced by sodium and boiling amyl alcohol, yielding small amounts of 2 : 4-*dimethylpiperidine*, $C_7H_{15}N$, which, after careful fractionation, has b. p. 136—138°. The *oxalate*, $C_9H_{17}O_4N,\frac{1}{2}H_2O$, crystallises in nacreous needles, m. p. 134°, after sintering at 130°. A small amount of *ε-hydroxy-γ-methylhexylamine*, $NH_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CHMe\cdot OH$, is also formed during the reduction; it has b. p. 119—120°/12 mm., and yields an *oxalate*, $C_{19}H_{19}O_5N$, with m. p. 142—145°. The amine reacts at 100—115° with a solution of hydrobromic acid saturated at below 0°, yielding an unsaturated *base* isomeric with dimethylpiperidine. It has b. p. 145—150°, and yields an *oxalate*, m. p. 150°. One of the formulæ $NH_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH\colon CHMe$ or

$$NH_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH\colon CH_2$$

is suggested.

Acetone does not condense with acraldehyde in the presence of hydrogen chloride; the only product appears to be mesityl oxide. The condensation takes place in the presence of a small amount of potassium cyanide, but the additive product formed polymerises with the greatest readiness. Definite products could not be isolated by condensing acraldehyde with ethyl acetoacetate in the presence of piperidine or potassium cyanide at −10°.

Ethoxypropaldehydediethylacetal and ethyl acetoacetate condense in the presence of glacial acetic acid and a little concentrated sulphuric acid or zinc chloride, yielding a product,

$$OEt\cdot CH_2\cdot CH_2\cdot CH\colon CAc\cdot CO_2Et,$$

with b. p. 142—144°/11 mm. This product is unsaturated, and readily decolorises solutions of bromine and permanganate.

Claisen's β-hydroxypentan-δ-one is formed when one-eighth of the amount of potassium cyanide recommended by Claisen is used for the condensation of aldehyde and acetone. Phosphorus tribromide reacts with an ethereal solution of the hydroxy-compound, yielding *β-bromopentan-δ-one*, $CH_3\cdot CHBr\cdot CH_2\cdot COMe$, with b. p. 50—55°/15 mm. The bromo-derivative is extremely unstable, and when kept for several days is transformed into a dark brown syrup. It condenses with ethyl sodiocyanoacetate, yielding ethyl α-cyano-γ-acetyl-β-methylbutyrate. J. J. S.

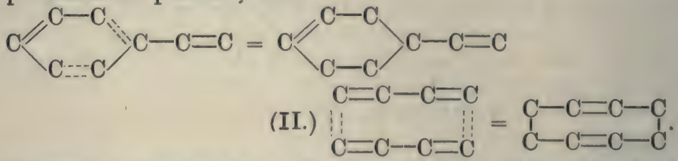
Catalytic Reactions at High Temperatures and Pressures. XX. Dehydration of Cyclic Alcohols. WLADIMIR N. IPATIEFF (*Ber.*, 1910, **43**, 3383—3387).—It has been shown previously (Abstr., 1903, i, 593; 1904, ii, 644; 1907, i, 6) that alcohols may be dehydrated in contact with alumina that has been only gently heated, ethers being formed at first, and then olefines.

Cyclic polyhydric alcohols may be dehydrated by heating with alumina in an atmosphere of hydrogen under a pressure of 39—40 atmospheres. Quinitol yields *cyclo*hexadiene with a little *cyclo*hexene at 350°, a good yield of the latter compound being obtained from *cyclo*hexanol. 1-Methyl*cyclo*hexan-2-ol yields methyl*cyclo*hexene in a mixture of several isomerides. Decahydro-β-naphthol yields octahydronaphthalene. C. H. D.

Polymerisation of Diethylene Hydrocarbons of the Type C:C·C:C. S. V. Lebedeff (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 949—961).—The polymerisation of hydrocarbons with a system of double bonds is so typical that it can be regarded as a general characteristic of these compounds; the temperature, however, greatly influences the velocity of the reaction and the character of the products; the latter, on the other hand, does not depend on the period of heating.

Two processes are possible, thus:

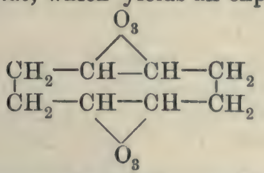
(I.) (II.)



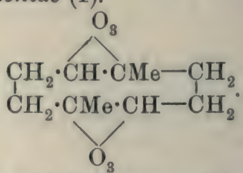
The lower the temperature the more is the 8-membered ring obtained. Light also favours process (II).

Divinyl heated in a sealed tube at 150° for six or seven days forms: (1) *Ethenyl*cyclo*hexene*, $\mathrm{CH}<\begin{smallmatrix}\mathrm{CH_2—CH_2}\\ \mathrm{CH—CH_2}\end{smallmatrix}>\mathrm{CH{\cdot}CH{:}CH_2}$, b. p. 66°/100 mm., 131°/760 mm., D_0^{20} 0·8321. When reduced with hydrogen in the presence of platinum-black, it yields ethyl*cyclo*hexane, b. p. 129—130° (Sabatier and Senderens give 128—129°). (2) A resin-like *polymeride*, which yields an explosive *ozonide* (I).

(I.)

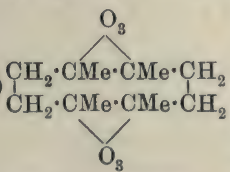


(II.)



Isoprene under similar conditions yields (1) dipentene. (2) A *hydrocarbon*, b. p. 44°/9 mm., 160—161°/760 mm., D_0^{20} 0·8331, for which the formula $\mathrm{CMe}<\begin{smallmatrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH—CH_2}\end{smallmatrix}>\mathrm{CMe{\cdot}CH{:}CH_2}$ is proposed; when reduced, it yields a *hydrocarbon*, $C_{10}H_{20}$, b. p. 164—165°/764 mm., D_0^{20} 0·799. (3) A resin-like *polymeride*, the *ozonide* of which has the constitution (II).

(III.)



Di-isoprene yields the *hydrocarbon*,

$$\mathrm{CMe}<\begin{smallmatrix}\mathrm{CH—CH_2}\\ \mathrm{CMe{\cdot}CH_2}\end{smallmatrix}>\mathrm{CMe{\cdot}CMe{:}CH_2},$$

b. p. 85°/13 mm., D_0^{20} 0·8598, and a resin-like *polymeride*, which yields the *ozonide* (III). Z. K.

Isomorphous Mixtures of Para-dihalogen Derivatives of Benzene. Nicolai N. Nagornoff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1159—1167).—1 : 4-Dichloro- and 1 : 4-di-iodo-benzene do not form solid solutions; their melting-point curve consists of two branches, with the eutectic point at 45° at the composition of 1·4 mol.% of the iodo-compound.

1 : 4-Dichloro- and 1 : 4-chloroiodo-benzene (m. p. 53°) form continuous isomorphous mixtures; their fusion curve passes through a minimum at 41° at the composition 50 mol.% of each compound.

1 : 4-Di-iodo- and 1 : 4-chloroiodo-benzene form solid solutions in one another. The saturated solution in chloroiodobenzene contains 20 mol.% of di-iodobenzene, whilst the saturated solution in the latter contains 15% of chloroiodobenzene. The curve consists of two branches, the eutetic point lying at 59° at the composition 14 mol.% of di-iodobenzene.

1 : 4-Dibromo- and 1 : 4-bromoiodo-benzene (m. p. 89·9°) form a continuous series of isomorphous mixtures; the minimum of their fusion curve is at 85·1°, corresponding with the composition of 60 mol.% of the dibromide.

1 : 4-Di-iodo- and 1 : 4-bromoiodo-benzene also form a continuous series of isomorphous mixtures, their curve passing through a minimum at about 100·5° at about 30 mol.% of di-iodo-benzene. Curves and tables are given for every pair of substances mentioned. Z. K.

Iodine Derivatives of Toluene. Henry L. Wheeler (*Amer. Chem. J.*, 1910, **44**, 493—507).—In papers on the action of iodine on *o*-, *m*-, and *p*-toluidines (Abstr., 1910, i, 17, 19, 662), an account has been given of 2 : 3-, 3 : 5-, and 2 : 5-di-iodotoluenes, 3 : 4 : 5-, 2 : 3 : 6-, and 3 : 4 : 6-tri-iodotoluenes, and 2 : 3 : 4 : 6-tetraiodotoluene. The study of the iodotoluenes has now been continued.

[With Charles A. Brautlecht.]—*5-Iodo-3-nitro-*o*-toluidine*,

$$NO_2 \cdot C_6H_2MeI \cdot NH_2,$$

m. p. 135°, prepared by the action of iodine chloride on 3-nitro-*o*-toluidine in presence of glacial acetic acid, forms orange needles. By the action of potassium iodide on the diazotisation product of this compound, *2 : 5-di-iodo-3-nitrotoluene*, $NO_2 \cdot C_6H_2MeI_2$, m. p. 95°, is obtained, which crystallises in colourless prisms, and on reduction with ferrous sulphate and ammonia is converted into *2 : 5-di-iodo-*m*-toluidine*, m. p. 82°, which forms pale brown prisms. When this substance is diazotised and the product treated with potassium iodide, 3 : 5 : 6-tri-iodotoluene is produced. *2 : 5-Di-iodoaceto-*m*-toluidide*,

$$C_6H_2MeI_2 \cdot NHAc,$$

m. p. 198—199°, forms long, colourless needles. When a mixture of 2 : 5-di-iodo-*m*-toluidine and iodine with ether, water, and calcium carbonate is warmed for eighteen hours, *2 : 5 : 6-tri-iodo-*m*-toluidine*, m. p. 119—120°, and 2 : 4 : 5 : 6-tetraiodo-*m*-toluidine are produced; the former crystallises in colourless needles, and when its diazotisation

product is treated with potassium iodide, 2 : 3 : 5 : 6-*tetraiodotoluene*, m. p. 125°, is obtained, which forms colourless needles.

4 : 5-*Di-iodo*-o-*toluidine*, $NH_2\cdot C_6H_2MeI_2$, m. p. 85°, prepared by the action of iodine or iodine chloride on *p*-iodo-*o*-toluidine, forms stout needles or long prisms. When its diazotisation product is treated with potassium iodide, 3 : 4 : 6-tri-iodotoluene (Abstr., 1910, i, 663) is obtained. 5-*Iodo*-4-*nitro*-o-*toluidine*, m. p. 109°, prepared by the action of iodine chloride on *p*-nitro-*o*-toluidine, forms long, bright yellow prisms. When its diazotisation product is treated with potassium iodide, 2 : 5-*di-iodo*-4-*nitrotoluene*, m. p. 117°, is obtained, which crystallises in buff-coloured, prismatic plates. This compound, on reduction with ferrous sulphate and ammonia, yields 2 : 5-*di-iodo*-p-*toluidine*, m. p. 109°, which forms buff-coloured prisms, and when diazotised and treated with potassium iodide is converted into 2 : 4 : 5-tri-iodotoluene, m. p. 118°, which is identical with the compound described by Neumann (Abstr., 1887, 573) as 2 : 4 : 6-tri-iodotoluene. 2 : 4 : 6-*Tri-iodotoluene*, m. p. 105°, prepared by the diazotisation of 2 : 4 : 6-tri-iodo-*m*-toluidine, crystallises in colourless needles.

[With Charles Hoffman.]—3-*Iodo*-5-*nitro*-o-*toluidine*, m. p. 173°, obtained by the action of iodine chloride on 5-nitro-*o*-toluidine in presence of glacial acetic acid, forms long, brown prisms. By the action of potassium iodide on the diazotisation product of this compound, 2 : 3-*di-iodo*-5-*nitrotoluene*, m. p. 143°, is produced, which crystallises in long, light brown, prismatic needles, and when reduced with ferrous sulphate and ammonia is converted into 5 : 6-*di-iodo*-m-*toluidine*, m. p. 106°, which forms large, brown crystals, but can be obtained in a colourless condition by distillation with steam. 5 : 6-*Di-iodo*-m-*acetotoluidide* has m. p. 208°. 3 : 5 : 6-*Tri-iodotoluene*, m. p. 72—73°, obtained by the action of potassium iodide on the diazotisation product of 5 : 6-di-iodo-*m*-toluidine, forms large, pale orange plates. On warming a mixture of 5 : 6-di-iodo-*m*-toluidine with iodine for several hours in presence of water, ether, and calcium carbonate, 4 : 5 : 6-*tri-iodo*-m-*toluidine*, m. p. 122°, and 2 : 4 : 5 : 6-*tetra-iodo*-m-*toluidine*, m. p. 205°, are produced, which crystallise in small needles. 4 : 5 : 6-*Tri-iodo*-m-*acetotoluidide*, m. p. 265° (decomp.), forms colourless needles. 2 : 3 : 4-*Tri-iodotoluene*, m. p. 92°, obtained by the diazotisation of 4 : 5 : 6-tri-iodo-*m*-toluidine, forms radiating crystals. By the action of potassium iodide on the diazotisation product of 4 : 5 : 6-tri-iodo-*m*-toluidine, 3 : 4 : 5 : 6-*tetraiodotoluene*, m. p. 284—285°, is obtained, which crystallises in straw-coloured needles. *Pentaiodotoluene*, m. p. 340° (decomp.), obtained by the action of potassium iodide on the diazotisation product of 2 : 4 : 5 : 6-tetraiodo-*m*-toluidine, forms small, dull yellow needles. E. G.

Auto-decomposition of Phenylnitromethane. Friedrich Heim (*Ber.*, 1910, 43, 3417—3420. Compare Dimroth, Abstr., 1910, i, 831).—In attempting to purify crude phenylnitromethane (Wislicenus and Endres, Abstr., 1902, i, 541) by distilling the crude product under diminished pressures, rapid decomposition ensued in one experiment, nitrous fumes were evolved, and a *product*, $C_{21}H_{17}ON$ (probably

triphenyldihydro*iso*oxazole), was obtained. This crystallises from alcohol, and has m. p. 138—139°. Other products were also formed.

In a second experiment, the crude product was subjected to steam distillation, and the phenylnitromethane obtained as a yellow oil; at the same time a small amount of a yellow solid was deposited in the condenser towards the end of the distillation, and dibenzhydroxamic acid was left in the flask.

Decomposition was also noticed when a specimen of phenylnitromethane, which has turned brown after exposure to light, was distilled.

It is suggested that the cause of the rapid decomposition is the presence of small amounts of phenylnitrolic acid in the crude material. J. J. S.

Nitro- and Amino-sulphobenzoic Acids. S. van Dorssen (*Rec. trav. chim.*, 1910, [ii], 14, 368—393).—In view of Taverne's statement (Abstr., 1906, i, 273) that *m*-sulphobenzoic acid on nitration furnishes 2-nitro-3-sulphobenzoic acid, whereas the symmetrical acid is to be expected, the author has re-investigated Taverne's acid and compared it with aminosulphobenzoic acids prepared in other ways. For the characterisation of the acids, the electrical conductivity and the solubility have been used. The results show that the acid prepared by Taverne is 3-nitro-5-sulphobenzoic acid. The conductivities quoted are for $v = 1200$ unless otherwise stated, and the solubilities are grams of acid in 100 grams of water, saturated at 25°.

4-Amino-2-sulphobenzoic acid, $\mu = 302\cdot4$, solubility 0·2997, crystallises in batons. 5-Amino-2-sulphobenzoic acid, $\mu = 332\cdot4$, solubility 0·1035, crystallises with $1H_2O$, and is unstable in aqueous solution. 4-Amino-3-sulphobenzoic acid, $\mu_{600} = 360\cdot0$, solubility 2·8346, was prepared by Fischer's method (Abstr., 1892, i, 331). Its constitution was established by the fact that aniline-*o*-sulphonic acid is formed with it as a by-product. 5-Nitro-3-sulphobenzoic acid, prepared from *m*-sulphobenzoic acid as described by Taverne, who wrongly assumed it to be the 2 : 3-isomeride, is identical with the acid prepared from *m*-nitrotoluene by sulphonation and subsequent oxidation of the CH_3- group, both acids furnishing *s*-dichlorobenzoic acid on treatment with phosphorus pentachloride. The nitro-acid, on reduction with tin and hydrochloric acid, furnishes the corresponding *amino-acid*, $\mu = 302\cdot4$, solubility 0·5745, and this gives no tribromoaniline with bromine water, a further proof of its symmetrical structure. 6-Amino-3-sulphobenzoic acid could not be obtained by sulphonating *o*-bromobenzoic acid and then replacing the bromine atom by $-NH_2$ by the action of ammonia, this reaction furnishing only aniline-*p*-sulphonic acid, $\mu_{128} = 93\cdot8$, which crystallises with 1 or 2 H_2O. 2-Amino-4-sulphobenzoic acid has $\mu = 356\cdot4$, solubility 1·0482, and shows a blue fluorescence in solution in water. 3-Amino-4-sulphobenzoic acid has $\mu_{1311\cdot2} = 382\cdot9$, solubility 0·0810. Attempts to prepare 2-amino-3-sulphobenzoic and 2-amino-5-sulphobenzoic acids were unsuccessful. The sulphonation of *m*-aminobenzoic acid gives rise to a mixture of 3-amino-4-sulphobenzoic and 5-amino-2-sulphobenzoic acids (compare Griess, this Journ., 1872, 717)

These acids are all considerably ionised in solution, and, as in the case of the aminobenzenesulphonic acids, the ionisation decreases for the isomerides in the order ortho → para → meta (for the relative positions of $-HSO_3$ and $-NH_2$), whilst in the case of the aminobenzoic acids it diminishes in the order meta → ortho → para. The difference is probably due to the tendency to form internal salts in the ortho- and para-compounds in the first case. T. A. H.

Sulphonation of Benzenesulphonic Acid. JULIUS J. POLAK (*Rec. trav. chim.*, 1910, [ii], 14, 416—446).—It is shown that in the sulphonation of benzenesulphonic acid, both meta- and para-disulphonic acids are formed, the former being the chief product. In sulphonating at high temperatures, some trisulphonic acid is produced.

Benzene-*o*-disulphonic acid was prepared from *o*-chloronitrobenzene by methods described by Blanksma (Abstr., 1900, i, 482) and by Wohlfahrt (Abstr., 1903, i, 203), the orthoanilic acid so obtained being converted into the *o*-disulphonic acid by Leuckart's method (Abstr., 1890, i, 603). The meta- and para-isomerides were prepared by similar processes, but as regards the second of these, a better yield was obtained by Gattermann's process (Abstr., 1899, i, 516), starting from aniline-*p*-sulphonic acid. The method of determining the relative proportions of the two isomerides formed in the sulphonation of benzenesulphonic acid consisted in determining the solidifying point of the mixed sulphonyl chlorides, these being produced quantitatively by a special process from the potassium salts of the mixed acids. For this purpose it was necessary to construct a table showing the solidifying points of mixtures of the two pure sulphonyl chlorides, and this is given in the original. It shows a transition point for the para-isomeride at 71·6°.

The barium salt was used for sulphonation, as this could be obtained dry, and the temperature was controlled by conducting the experiments in vessels surrounded by vapours of substances boiling at the required temperatures.

Tables showing the relative percentages of the two disulphonic acids formed after various intervals, (*a*) with fuming sulphuric acid of known composition, (*b*) with 98% acid, that is, in presence of water, are given. At 183°, sulphonation is incomplete, whilst at 233° some trisulphonic acid is formed, but complete sulphonation to disulphonic acids takes place at 209°. It appears that meta- and para-acids are both formed initially, and that reciprocal transformation of both acids may then go on, the change para ⟶ meta being more rapid than the reverse one at 209°, but both are very slow, although they are accelerated by rise of temperature and by the presence of water. T. A. H.

Preparation of Certain Sulphonic Acids in the Free State. JOSEPH H. KASTLE (*Amer. Chem. J.*, 1910, 44, 483—487).—A simple method is described for the preparation of certain sulphonic acids by precipitating them from concentrated aqueous solutions by the addition of another strong acid, such as hydrochloric or sulphuric acid.

p-Nitro-*o*-toluenesulphonic acid can be prepared in a pure state in the following manner. *p*-Nitrotoluene is treated with fuming sulphuric acid, and the product is poured into an equal volume of water.

On cooling, the sulphonic acid separates in crystals, and is collected, dissolved in a small quantity of water, precipitated by the addition of concentrated hydrochloric acid, and recrystallised several times from water. The acid is thus obtained in pale yellow prisms containing $2H_2O$, and not $2\frac{1}{2}H_2O$ as stated by Jenssen (Abstr., 1874, 479).

In a similar way, a toluenesulphonic acid, probably the para-compound, can be prepared, which forms colourless, prismatic crystals, containing $1H_2O$.

Attempts have been made to isolate benzenesulphonic and *o*-nitrotoluenesulphonic acids by this method, but without success. E. G.

Catalytic Reactions at High Temperatures. XXI. Influence of Foreign Substances on the Activity of Catalysts. Wladimir N. Ipatieff (*Ber.*, 1910, 43, 3387—3393).—Hydroaromatic compounds containing a double linking in the ring are completely reduced when heated with copper and hydrogen in an iron vessel, but when the vessel is of copper or phosphor-bronze, the reduction does not extend to this linking. Further experiments show that amylene is completely reduced at 300° in an iron tube in presence of copper oxide, but that no reduction occurs in the absence of the copper oxide, whilst in presence of copper or copper oxide, enclosed in a copper tube, the reduction is very incomplete, the reaction $C_5H_{10} + H_2 \rightleftarrows C_5H_{12}$ being reversible.

Using copper oxide in an iron tube, octahydronaphthalene is partly reduced to decahydronaphthalene, and partly decomposed, yielding *cyclo*hexane. The copper walls of the vessel may hinder the reaction, or it may be necessary that two catalysts should be simultaneously present. Further experiments are in progress. C. H. D.

Action of Metals on Aromatic Keto-chlorides and the Properties of Compounds of the Type $R_2CCl\cdot CClR_2$. James F. Norris, Ruth Thomas, and B. Marion Brown (*Ber.*, 1910, 43, 2940—2959. Compare Schmidlin and Escher, Abstr., 1910, i, 369).—In compounds of the type CR_2Cl_2, when the substituting radicle is positive or strongly negative, the halogen atom only reacts with difficulty with metals and certain metallic oxides; but on passing from the positive end of the series to the negative, the reactivity increases until keto-chlorides are obtained which readily part with chlorine. If the negative character of the substituting group is increased from this point, the compounds become stable again; for example, mercury only eliminates one halogen from benzophenone chloride, forming tetraphenylethylene dichloride; 4 : 4′-dichlorobenzophenone chloride and mercury yield a mixture of tetrachlorotetraphenylethylene and tetraphenylethylene; 2 : 4′-dichlorobenzophenone chloride gives exclusively tetrachlorotetraphenylethylene, whilst 2 : 5 : 2′ : 5′-tetrachlorobenzophenone chloride does not interact either with mercury or with zinc. Both zinc and silver act rapidly on benzophenone chloride, forming tetraphenylethylene.

Sulphuryl chloride in presence of small quantities of acetic acid was found to afford an effective means of causing the addition of chlorine to double linkings, and it is possible to obtain tetraphenylethylene

dichloride in this manner. This substance forms characteristic additive compounds with carbon tetrachloride and chloroform.

When tetraphenylethylene dichloride is slowly heated (compare Schmidlin and Escher, *loc. cit.*), the chief product is 4-chlorotetraphenylethylene. At higher temperatures, tetraphenylethylene is formed. With magnesium phenyl bromide, 4-phenyltetraphenylethylene is formed in addition to tetraphenylethylene.

Tetraphenylethylene dibromide could not be obtained by the action of metals on benzophenone bromide tetraphenylethylene being the sole product of the reaction. Tetraphenylethylene dichloride when heated with bromobenzene and sodium also yields tetraphenylethylene.

By the action of aluminium chloride on 4 : 4′ : 4″ : 4‴-tetrachlorotetraphenylethylene dichloride, 9 : 10-diphenylphenanthrene and a tetrachloro-substitution product are obtained ; the para-hydrogen atoms take no part in the reaction.

Both triphenylmethyl and pentaphenylethane react with sulphuryl chloride, forming triphenylmethyl chloride in each instance ; tetraphenylethane and sulphuryl chloride do not interact. Sulphuryl chloride converts triphenylcarbinol into triphenylmethyl chloride, and its trinitro-derivative into trinitrotriphenylmethyl chloride.

4 : 4′ : 4″ : 4‴-*Tetrachlorotetraphenylethylene* has m. p. 216—217° ; the *dichloride* has m. p. 190—191°. Fluorenone chloride crystallises in long, straw-yellow needles, m. p. 101·5—102·5°. Silver converts it into bisdiphenylene ethylene ; mercury into *dibiphenylene-ethylene dichloride*, which crystallises in colourless needles, m. p. 228—236°, to a red liquid.

4-*Phenylbenzophenone chloride* forms crystals, m. p. 45—47°. When boiled with diphenylmethane, 4-*phenyltetraphenylethylene* is formed, m. p. 189—190°. A *tetranitro*-derivative forms yellow crystals, m. p. 278—280°.

Convenient methods are described for the preparation of benzophenone, tetraphenylethylene, etc., on a large scale. E. F. A.

Gradual Synthesis of the Benzene Chain. MAURICE DELACRE (*Bull. Soc. chim.*, 1910, [iv], 7, 1041—1046. Compare Abstr., 1910, i, 120, 323).—A paper detailing the steps in the synthesis of triphenylbenzene from acetophenone, through dypnone, CMePh:CHBz, and dypnopinacone, $\begin{matrix} CH_2\cdot CPh:CH\cdot CPh\cdot OH \\ | \qquad\qquad\qquad | \\ CH_2\cdot CPh:CH\cdot CPh\cdot OH \end{matrix}$. The latter, like the members of the homodypnopinacone and *iso*dypnopinacolin groups, furnishes readily the hydrocarbon, $C_{25}H_{22}$, the reduction product of which gives triphenylbenzene, allylbenzene, and ethylbenzene on heating. The remainder of the paper is devoted to discussing the bearing of this and other reactions among pinacolin derivatives, on the general question of the gradual synthesis of the benzene chain. T. A. H.

Bromo-salts of Platinum. ALEXANDER GUTBIER [with FR. BAURIEDEL and C. J. OBERMAIER] *Ber.*, 1910, **43**, 3228—3234. Compare Abstr., 1910, i, 12).—Various substituted ammonium platinibromides have been prepared by adding a solution of the substituted

ammonium bromide to a solution of hydrogen platinibromide. The resulting precipitates were purified by recrystallisation from aqueous hydrobromic acid. In some cases there was a tendency for decomposition to take place when aqueous solutions were used, a resin being formed; this tendency could be obviated by using dilute alcoholic solutions of the substituted ammonium bromide and of hydrogen bromide.

Phenylammonium platinibromide, $(NH_3Ph)_2PtBr_6$: yellowish-red, felted crystals, which are still solid at 260°. *Phenylmethylammonium platinibromide*, $(NH_2MePh)_2PtBr_6$: bright red, rhombic needles, m. p. 227—228° (decomp.). *Phenyldimethylammonium platinibromide*,

$(NHMe_2Ph)_2PtBr_6$:

red needles. *Phenylethylammonium platinibromide*,

$(NH_2EtPh)_2PtBr_6$:

bright red, microscopic needles, m. p. 209—210°. *Phenyldiethylammonium platinibromide*, $(NHEt_2Ph)_2PtBr_6$: bright red, prismatic crystals. o-*Tolylammonium platinibromide*, $(NH_3 \cdot C_6H_4Me)_2PtBr_6$: bright yellowish-red needles, probably monoclinic, m. p. 225—226° (decomp.). m-*Tolylammonium platinibromide*,

$(NH_3 \cdot C_6H_4Me)_2PtBr_6$:

bright red, shining crystals, m. p. 266° (decomp.). p-*Tolylammonium platinibromide*, $(C_6H_4Me \cdot NH_3)_2PtBr_6$: shining, yellowish-red, flat prisms, m. p. 268—269°. 1:2:4-*Xylylammonium platinibromide*,

$(C_6H_3Me_2 \cdot NH_3)_2PtBr_6$:

bright red, felted, rhombic needles, m. p. 262—263°. 1:3:4-*Xylylammonium platinibromide*: yellowish-red needles and plates, m. p. 256°. 1:4:5-*Xylylammonium platinibromide*: red, monoclinic needles or rhombic plates, m. p. 241°. *Pyridinium platinibromide*,

$(PyH)_2PtBr_6$:

shining, reddish-brown needles, which are still solid at 270°. *a-Picolinium platinibromide*, $(C_5NH_5Me)_2PtBr_6$: red or reddish-brown, rhombic plates, m. p. 211—212°. *Quinolinium platinibromide*, $(C_9NH_8)_2PtBr_6$: bright red, monoclinic prisms, m. p. 254—255° (decomp.). *Benzylammonium platinibromide*, $(NH_3 \cdot C_7H_7)_2PtBr_6$: yellowish-red, rhombic plates, m. p. 257—259° (decomp.). *Benzylethylammonium platinibromide*, $(NH_2Et \cdot C_7H_7)_2PtBr_6$: bright red plates and needles, m. p. 177°. *Benzidinium platinibromide*,

$[N_2H_6(C_6H_4)_2]PtBr_6$:

yellowish-red monoclinic, needles, which are strongly pleochroic. o-*Phenylenediammonium platinibromide*, $[C_6H_4(NH_3)_2]PtBr_6$, brownish-yellow, monoclinic, pleochroic needles or plates. m-*Phenylenediammonium platinibromide*: dark red, rhombic needles, which do not melt at 270°. p-*Phenylenediammonium platinibromide*: dark red, monoclinic prisms, slightly pleochroic. *a-Naphthylammonium platinibromide*, $(C_{10}H_7 \cdot NH_3)_2PtBr_6$: red, monoclinic crystals, which do not melt at 270°. *β-Naphthylammonium platinibromide*, reddish-yellow plates and prisms, which are still solid at 275°.

The above compounds are only very slightly soluble in cold water, giving yellow solutions; they are more soluble in hot water to yellowish-red or red solutions.

T. S. P.

Hydroxy- and Dihydroxy-phenylalkylammonium Compounds, and β-Nitrostyrenes. KARL W. ROSENMUND (*Ber.*, 1910, **43**, 3412—3417).—Attempts have been made to synthesise compounds analogous to hordenine alkylhalides (compare Abstr., 1910, i, 241), the method of procedure consisting in the complete methylation of the alkyl ethers of the base, and then removal of the alkyl group of the phenolic ether by means of hydriodic acid. p-*Methoxyphenyl*iso*propyltrimethylammonium iodide*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot CHMe\cdot NMe_3I,$$

obtained by methylating *p*-methoxyphenyl*iso*propylamine, crystallises from water in long, colourless needles, m. p. 215—216°, and when boiled with hydriodic acid yields p-*hydroxyphenyl*iso*propyltrimethylammonium iodide* in the form of colourless needles, m. p. 241—242°. 3 : 4-*Dimethoxyphenyl*iso*propyltrimethylammonium iodide*,

$$C_6H_3(OMe)_2\cdot CH_2\cdot CHMe\cdot NMe_3I,$$

forms colourless crystals, m. p. 187°, and the corresponding *dihydroxy*-derivative crystallises from alcohol in colourless, compact prisms, m. p. 190°, and its aqueous solution gives the catechol reaction with ferric chloride.

A good yield of β-nitromethylenedioxystyrene (Bouveault and Wahl, *Bull. Soc. chim.*, 1903, [iii], **29**, 523 ; Medinger, *Monatsh.*, 1906, **27**, 244) is obtained by the gradual addition of a methyl-alcoholic solution of potassium hydroxide (1·5 mols.) to an alcoholic solution of piperonal and nitromethane, and then pouring the whole into an excess of ice-cold 10% hydrochloric acid. When reduced with zinc dust and a mixture of alcohol and glacial acetic acid, the nitro-compound yields homopiperonylaldoxime, m. p. 119—120°, and this when reduced with 3% sodium amalgam yields homopiperonylamine, the hydrochloride of which has m. p. 208° (Medinger, Abstr., 1906, i, 421, gives 197°).

β-Nitrodimethoxystyrene, $C_6H_3(OMe)_2\cdot CH:CH\cdot NO_2$, obtained from veratraldehyde and nitromethane, crystallises in yellow plates, m. p. 140°.

Veratraldehyde is easily prepared by methylating vanillin with methyl sulphate at 65—70° in the presence of 10% aqueous potassium hydroxide solution (compare Perkin and Robinson, Trans., 1907, **91**, 1079 ; Decker and Koch, Abstr., 1908, i, 35). J. J. S.

Action of Cyanogen Bromide on Tertiary Bases containing the Phenylethyl and Phenylpropyl Groups. JULIUS VON BRAUN (*Ber.*, 1910, **43**, 3209—3220. Compare Abstr., 1910, i, 189, 506).—It has been shown previously that groups containing an unsaturated linking in the βγ-position are, in general, more readily removed from amines by the action of cyanogen bromide than saturated groups. In order to ascertain if a similar influence is to be observed in the case of groups containing unsaturated linkings in more remote positions, the author has investigated the behaviour towards cyanogen bromide of tertiary amines of the following types: $CH_2Ph\cdot CH_2\cdot NR_2$ and $CH_2Ph\cdot CH_2\cdot CH_2\cdot NR_2$, and finds that the groups are more firmly attached as the length of the aliphatic chain increases.

Di-β-phenylethyl-dimethylammonium bromide,
$NMe_2(CH_2\cdot CH_2Ph)_2Br$,
soft, fatty leaflets, m. p. 160°, is obtained together with β-phenylethyldimethylamine, $NMe_2\cdot CH_2\cdot CH_2Ph$, b. p. 205°/760 mm. (compare Barger, Trans., 1909, 95, 2193), by the action of β-phenylethyl bromide on dimethylamine.

Cyanogen bromide reacts vigorously with β-phenylethyldimethylamine, yielding *β-phenylethyltrimethylammonium bromide*,
$CH_2Ph\cdot CH_2\cdot NMe_3Br$,
m. p. 220°, β-phenylethyl bromide, and *β-phenylethylmethylcyanamide*, $CH_2Ph\cdot CH_2\cdot NMe\cdot CN$. The latter has b. p. 164—165°/10 mm., and is hydrolysed by sulphuric acid in aqueous alcoholic solution to *as*-β-phenylethylmethylcarbamide, $C_2H_4Ph\cdot NMe\cdot CO\cdot NH_2$; energetic hydrolysis yields β-phenylethylmethylamine, $NHMe\cdot C_2H_4Ph$ (compare Johnson and Guest, Abstr., 1909, i, 794).

Phenyl-β-phenylethylmethylamine, $NMePh\cdot C_2H_4Ph$, obtained from β-phenylethyl bromide and methylaniline, is a pale yellow liquid, b. p. 198—199°/18 mm., and solidifies in ice to a snow-white mass, m. p. 44°; it yields a *picrate*, m. p. 101°, and a *platinichloride*, m. p. 162—163° (decomp.); when treated with cyanogen bromide, it yields *β-phenylethylphenylcyanamide*, $C_2H_4Ph\cdot NPh\cdot CN$, b. p. 220—225°/11 mm. (slight decomp.), together with methyl bromide and β-phenylethyl bromide.

β-Phenylethyldiethylamine, $NEt_2\cdot C_2H_4Ph$, prepared by heating β-phenylethyl bromide with diethylamine, is a colourless, almost odourless liquid, b. p. 103°/10 mm., and gives a crystalline *picrate*, m. p. 95°, and an oily *platinichloride*, which slowly solidifies, m. p. 140°; when heated with cyanogen bromide, it yields β-phenylethyl bromide and *β-phenylethylethylcyanamide*, $C_2H_4Ph\cdot NEt\cdot CN$, which has b. p. 174°/15 mm., and is hydrolysed by sulphuric acid to *β-phenylethylethylamine*, $NHEt\cdot C_2H_4Ph$, a colourless oil, b. p. 99—100°/13 mm.; the latter gives an oily *platinichloride*, which slowly solidifies, and a crystalline *picrate*, m. p. 130°, a *phenylthiocarbamide*, $C_2H_4Ph\cdot NEt\cdot CS\cdot NHPh$, m. p. 88°, and a *carbamide*,
$C_2H_4Ph\cdot NEt\cdot CO\cdot NH_2$,
m. p. 58°; the *benzoyl* and *benzenesulphonyl* derivatives are oils.

γ-Phenylpropyldimethylamine (Senfter and Tafel, Abstr., 1894, i, 579) is obtained by the interaction of γ-phenylpropyl chloride or bromide with dimethylamine.

The action takes place more readily with the bromide, but is accompanied by the formation of an oily quaternary *bromide*,
$NMe_2(C_3H_6Ph)_2Br$,
which is converted by silver chloride into the corresponding *chloride*, m. p. 88°.

γ-Phenylpropyldimethylamine reacts vigorously with cyanogen bromide, yielding γ-phenylpropylmethylcyanamide and *γ-phenylpropyltrimethylammonium bromide*, $CH_2Ph\cdot CH_2\cdot CH_2\cdot NMe_3Br$, which forms a red, crystalline *platinichloride*, m. p. 205—209°.

γ-Phenylpropylmethylcyanamide, $C_3H_6Ph\cdot NMeCN$, b. p. 187—189°/17 mm., forms a colourless liquid, and is hydrolysed with difficulty. On heating for several hours at 170° with strong hydrochloric acid, it

is converted into *γ-phenylpropylmethylamine*, $NHMe{\cdot}C_3H_6Ph$, a colourless oil, b. p. 110°/17 mm., which gives an oily *picrate* and a crystalline *platinichloride*, m. p. 188°; the *carbamide*, $C_3H_6Ph{\cdot}NMe{\cdot}CO{\cdot}NH_2$, crystallises in leaflets, m. p. 101°.

The direct interaction of γ-phenylpropyl chloride or bromide and methylamine furnishes a very small yield of γ-phenylpropylmethylamine.

γ-Phenylpropyldiethylamine, $NEt_2{\cdot}C_3H_6Ph$, prepared from γ-phenylpropyl bromide and diethylamine, is a colourless liquid, b. p. 137—139°/22 mm., giving an oily *picrate* and *platinichloride*. It is converted by the action of cyanogen bromide into a mixture of γ-phenylpropyl bromide, diethylcyanamide, and *γ-phenylpropylethylcyanamide*,

$$C_3H_6Ph{\cdot}NEt{\cdot}CN.$$

The latter has b. p. 191—192°/14 mm., and is hydrolysed by hydrochloric acid into *γ-phenylpropylethylamine*, a colourless liquid, b. p. 118°/16 mm.

γ-Phenylpropyldipropylamine, $NPr^{\alpha}_2{\cdot}C_3H_6Ph$, obtained from γ-phenylpropyl bromide and dipropylamine, is a colourless, almost odourless liquid, b. p. 158—160°/17 mm.; the *picrate* is an oil; the *platinichloride* has m. p. 91—93°. It reacts vigorously with cyanogen bromide, yielding propyl bromide, γ-phenylpropyl bromide, and *γ-phenylpropylpropylcyanamide*, $C_3H_6Ph{\cdot}NPr^{\alpha}{\cdot}CN$, b. p. 200°/16 mm. The latter is hydrolysed by hydrochloric acid into *γ-phenylpropylpropylamine*, $NHPr^{\alpha}{\cdot}C_3H_6Ph$, a colourless, odourless liquid, b. p. 134°/17 mm., which forms an orange-yellow, crystalline *picrate*, m. p. 97°, and an oily *platinichloride*. F. B.

Isomerism of Anils (Schiff's Bases). III. WILHELM MANCHOT (*Ber.*, 1910, **43**, 3359—3362).—Reply to Anselmino (Abstr., 1910, i, 462), who has not appreciated the fact that the object of the molecular-weight determinations by Manchot and Furlong (Abstr., 1909, i, 805; 1910, i, 33) is to ascertain whether the entire differences between the two forms of an anil may not be due to differences in molecular magnitude. The existence of a temperature limit, stated by Anselmino, above and below which the two forms of an anil are stable respectively, is disproved by the fact that the yellow form of *p*-bromosalicylaldehydeanil separates from solutions at temperatures much higher than 33°, the limit set by Anselmino. C. S.

Sulphanilide. ALFRED WOHL and FRANZ KOCH (*Ber.*, 1910, **43**, 3295—3307).—A good yield of sulphanilide (W. Traube, Abstr., 1891, 569) can be obtained by dropping a solution of sulphuryl chloride dissolved in dry ether into an excess of aniline dissolved in about three times its volume of dry ether and cooled by a good freezing mixture. The yield is 60% of the theoretical, and the by-product is azobenzene. When chloroform or carbon tetrachloride is used as diluent, Mohr's trianilinobenzene (Abstr., 1890, 614) is formed. The anilide is not readily hydrolysed, and is not affected when heated with sodium ethoxide at 180°.

The *disodium* salt, $C_{12}H_{10}O_2N_2SNa_2$, crystallises on the addition of

benzene and light petroleum to its alcoholic solution in slender, glistening needles containing alcohol. The *acetyl* derivative,

$$NPhAc\cdot SO_2\cdot NHPh,$$

prepared by the action of acetic anhydride and a little sulphuric acid at the ordinary temperature, forms compact, rhombic prisms, m. p. 158—159°, after sintering at 155°, and dissolves in alkalis. The *diacetyl* derivative, $SO_2(NAcPh)_2$, obtained by using a temperature of 45°, crystallises from carbon tetrachloride in prismatic needles, m. p. 164°, after sintering at 159°. This compound is decomposed readily when heated with acetic anhydride, yielding diacetanilide and sulphuric acid, but at the same time the sulphuric acid reacts with the acetylsulphonamic acid, which is an intermediate product, yielding acetylaniline-*p*-sulphonic acid:

$$SO_2(NPhAc)_2 \longrightarrow NPhAc\cdot SO_3H \longrightarrow NHAc\cdot C_6H_4\cdot SO_3H.$$

Diphenyldimethylsulphamide, $SO_2(NPhMe)_2$, obtained by the action of methyl iodide and sodium methoxide at 100°, crystallises in prismatic needles or plates, m. p. 96—97°, and is also formed when silver oxide and methyl iodide are used.

An explosive *dinitroso*-derivative, $SO_2(NPh\cdot NO)_2$, is formed when nitrous fumes are passed into a dry ethereal solution of the anilide. It forms hygroscopic crystals, which explode at 73—74°. Ethereal or chloroform solutions of the nitroso-derivative, and also of the nitroso-derivative of 4 : 4′-dibromosulphanilide, condense with β-naphthol, yielding azo-derivatives and black azo-dyes, which have not been obtained pure.

A solution of sulphanilide in sodium carbonate reacts with an excess of a diazotised solution of *p*-nitroaniline, yielding a brownish-black dye.

2 : 4 : 2′ : 4′-*Tetranitrodiphenylsulphamide*, $SO_2[NH\cdot C_6H_3(NO_2)_2]_2$, prepared by adding the sulphamide or, still better, its mono- or diacetyl derivative to fuming nitric acid cooled to 0°, separates as well developed prisms, m. p. 183°, and is decomposed when boiled with water. Fuming nitric acid reacts with a well cooled sulphuric acid solution of the anilide, yielding *o*-nitroaniline-*p*-sulphonic acid. A chloroform solution of bromine converts the anilide into its 4 : 4′-*dibromo*-derivative, $C_{12}H_{10}O_2N_2Br_2S$, in the form of plates, m. p. 124—125°. The bromo-derivative reacts with sodium acetate and acetic anhydride, yielding *p*-bromoacetanilide. When further brominated, the dibromo-derivative yields 2 : 4 : 4′-*tribromodiphenylsulphamide*, $C_{12}H_9O_2N_2Br_3S$, which crystallises from benzene in tetragonal pyramids, m. p. 143°.

Sulpho-p-*toluidide*, $C_{14}H_{16}O_2N_2S$, obtained when a chloroform solution of sulphonyl chloride is added to a well cooled solution of *p*-toluidine in dry chloroform, crystallises from carbon tetrachloride or light petroleum in colourless, prismatic needles, m. p. 96—97°.

Nitroanilines, acetanilide, and aniline hydrochloride do not react with sulphuryl chloride, and monomethylaniline yields dark brown dyes. J. J. S.

Comparative Nitration of Mono- and Diacylated Aromatic Amines. FRÉDÉRIC REVERDIN and ARMAND DE LUC (*Ber.*, 1910, **43**, 3460—3464; *Compt. rend.*, 1910, **151**, 985. Compare Abstr., 1909, i, 377, 913).—A comparative examination of the nitration of a few

acylated and diacylated aromatic amines has been undertaken in order to ascertain what influence is exerted on the stability of the molecule by the second acyl group attached to the nitrogen atom, and what orientating effect it has on the entrant nitro-group. The experimental results are given only in the paper in the *Berichte*.

As already recorded, 2 : 3-dinitro-4-toluenesulphonylaminoanisole is obtained when 1 part of 4-toluenesulphonylaminoanisole in 10 parts of glacial acetic acid is added to 5 parts of nitric acid, D 1·52, between 20—30°; under the same conditions, 4-acetyltoluenesulphonylamino-anisole is unchanged. When, however, using the same proportions, the temperature is allowed to rise to 60°, the first substance behaves as before, whilst the diacylated compound yields 3-*nitro*-4-*acetyltoluenesulphonylaminoanisole*, $OMe\cdot C_6H_3(NO_2)\cdot NAc\cdot SO_2\cdot C_7H_7$, m. p. 197°. Finally, when the monoacylated compound is added to the nitric acid below 20°, and the mixture, after being heated momentarily to 55°, is poured into water, the 2 : 3-dinitro-compound is obtained, together with the 3-nitro-compound. Under the same conditions (except that the temperature can be raised to 65° before gas is evolved), the diacylated compound yields 2 : 5-*dinitro*-4-*acetyltoluenesulphonylaminoanisole*, m. p. 169°, yellow leaflets, and the 2 : 3-dinitro-*isomeride*, m. p. 205°, colourless needles, which are soparated by the greater solubility of the former in hot alcohol.

3-Nitroaceto-*p*-toluidide is formed when aceto-*p*-toluidide in acetic acid is added to nitric acid below 15° and the temperature is then raised gradually to 65°; the same compound is also formed when diaceto-*p*-toluidide is treated similarly, the temperature being raised, however, only to 20° (evolution of gas). When nitrated by nitric acid alone, aceto-*p*-toluidide at 65° (evolution of gas) yields 38% of 3 : 5-dinitro-aceto-*p*-toluidide and 62% of 3-nitroaceto-*p*-toluidide, whilst diaceto-*p*-toluidide must be cooled by ice during the nitration, and yields 3-nitro-*p*-toluidine.

When nitrated in acetic acid solution, 4-toluenesulphonylamino-toluene at 70° yields 80% of 3 : 5-*dinitro*-4-*toluenesulphonylaminotoluene*, $C_6H_2Me(NO_2)_2\cdot NH\cdot SO_2\cdot C_7H_7$, m. p. 204° (the same substance is also produced at 40° in the absence of the acetic acid), whilst 4-*acetyltoluenesulphonylaminotoluene*, $C_6H_4Me\cdot NAc\cdot SO_2\cdot C_7H_7$, m. p. 134°, obtained from 4-toluenesulphonylaminotoluene and acetic anhydride, is not nitrated, even at 75°; when, however, the diacylated compound is treated below 15° with nitric acid alone, the temperature being raised subsequently to 40° (evolution of gas), 2-*nitro*-4-*nitrotoluenesulphonylaminotoluene*, $NO_2\cdot C_6H_3Me\cdot NH\cdot SO_2\cdot C_7H_6\cdot NO_2$, m. p. 183°, is obtained, which yields 2-nitro-*p*-toluidine by hydrolysis.

From the preceding experiments, it seems that the presence of the acetyl and the toluenesulphonyl groups increases the stability of the molecule, and, in the case of *p*-toluidine, affects the orientation of the nitro-group and facilitates the introduction of a nitro-group into the toluenesulphonyl nucleus; the presence of two acetyl groups in *p*-toluidine apparently diminishes the stability of the molecule. C. S.

Action of Phenylthiocarbimide on Mono- and Di-*iso*amyl-aniline. Theodor St. Warunis (*Ber.*, 1910, 43, 2972—2976).—By the

action of phenylthiocarbimide on mono*iso*amylaniline, *diphenylisoamylthiocarbamide*, $NHPh\cdot CS\cdot NPh\cdot C_5H_{11}$, is formed; the same compound is obtained from crude di*iso*amylaniline, owing to the mono-derivative present as impurity. It crystallises in large, transparent, colourless needles, m. p. 107·5°, and sublimes at 240—250°.

To determine sulphur in organic substances, they are heated with a mixture of potassium hydroxide and sodium peroxide in a silver crucible, at first at 75—85°, and subsequently over a small flame.

E. F. A.

Some Derivatives of 3 : 4 : 5-Trinitro-2-methoxytoluene. JAN J. BLANKSMA (*Rec. trav. chim.*, 1910, **29**, 410—415).—The 3 : 4 : 5-trinitro-2-methoxytoluene was prepared by the nitration of 4-nitro-2-methoxytoluene (Kaufler and Wenzel, Abstr., 1901, i, 590). When treated with ammonia, it yields chiefly 3 : 5-*dinitro*-2-*methoxy*-p-*toluidine* as yellow crystals, m. p. 130°, the *acetyl* derivative of which melts at 220°.

By the diazotisation of 3 : 5-dinitro-2-methoxy-*p*-toluidine, colourless crystals of 3 : 5-dinitro-2-methoxytoluene are produced; when treated with ammonia, this is transformed into 3 :5-dinitro-*o*-toluidine. On heating 3 : 4 : 5-trinitro-2-methoxytoluene with ammonia in a sealed tube, dark brown crystals of 3 : 5-dinitro-2 : 4-tolylenediamine, m. p. 254°, are formed; Nietzki and Rösel found 300° as the melting point of this substance (Abstr., 1891, 192); its *acetyl* derivative does not melt below 300°.

3 : 5-*Dinitro*-2 : 4-*di*(*methylnitroamino*)*toluene* forms colourless crystals, m. p. 169°; 2-*chloro*-5-*nitro*-4-*aceto*-p-*toluidide* crystallises in pale yellow crystals, m. p. 112°.

N. C.

Quinol Di*iso*butyl Ether. RUDOLF NIETZKI and KESSELRING (*Ber.*, 1910, **43**, 3459—3460).—Attempts to prepare Schubert's tetranitroquinol di*iso*butyl ether (Abstr., 1883, 60) have resulted in the preparation of only a *trinitro*-compound, $C_{14}H_{19}O_8N_3$, m. p. 96°, even when fuming nitric acid and high temperatures have been employed.

C. S.

Phenols Insoluble in Alkalis. HENRY A. TORREY and ROGER ADAMS (*Ber.*, 1910, **43**, 3227—3228. Compare Abstr., 1907, i, 325; 1908, i, 460).—Of the isomeric nitrophenylhydrazones of paenol and bromopaenol, only the para-compounds are soluble in aqueous sodium hydroxide.

Paeonol-o-*nitrophenylhydrazone*,

$$OH\cdot C_6H_3(OMe)\cdot CMe\colon N\cdot NH\cdot C_6H_9\cdot NO_2,$$

crystallises in deep red, monoclinic prisms, m. p. 217°; the m-*nitro*-derivative in red lamellæ, m. p. 197°, and the p-*nitro*-derivative in red crystals, m. p. 235—236° (decomp.).

Bromopaeonol-o-*nitrophenylhydrazone* forms red needles, m. p. 253—254°; the m-*nitrophenylhydrazone*, brownish-red lamellæ, m. p. 208°, and the p-*nitro*-derivative, orange needles, m. p. 222°.

F. B.

***p*-Aminothiophenol [*p*-Aminophenyl Mercaptan]. II.** THEODOR ZINCKE and P. JÖRG (*Ber.*, 1910, **43**, 3443—3450. Compare Abstr., 1909, i, 789).—*p*-Methylthiolaniline (*p*-aminophenyl methyl sulphide)

resembles aniline in many of its reactions, for example, it reacts with quinones, yielding intensely coloured anilino-derivatives, it condenses with 1-chloro-2 : 4-dinitrobenzene, yielding a substituted diphenylamine derivative, and yields diazonium salts which are readily transformed into corresponding chloro- and cyano-derivatives.

Dimethylthiolanilino-p-*benzoquinone*, $C_6H_2O_2(NH\cdot C_6H_4\cdot SMe)_2$, prepared by boiling an alcoholic solution of the aminothiophenol with *p*-benzoquinone for a short time, separates from tetrachloroethane as a finely crystalline powder, and dissolves in concentrated sulphuric acid to a deep bluish-green solution. The *derivative* from α-naphthaquinone, $C_6H_4<\begin{matrix}CO\cdot CH\cdot NH\cdot C_6H_4\cdot SMe\\ \| \\ CO\cdot CH\end{matrix}$, crystallises from hot alcohol in dark red, glistening plates with a metallic lustre, and has m. p. 164—165°; when boiled with alkalis it is slowly decomposed, and yields hydroxynaphthaquinone. The isomeric *compound* from β-naphthaquinone, $C_6H_4<\begin{matrix}CO-C(OH)=CH\\ C(:N\cdot C_6H_4\cdot SMe)\end{matrix}>$, crystallises from a mixture of alcohol and glacial acetic acid in brownish-red plates, and needles with a golden-yellow lustre, and has m. p. 242—243°. Its solution in concentrated sulphuric acid has a brownish-violet colour. It is more stable than the corresponding dianilino-derivative of β-naphthaquinone, and is not transformed so readily into derivatives of α-naphthaquinone.

2 : 4-*Dinitro*-4′-*methylthioldiphenylamine*, $C_6H_3(NO_2)_2\cdot NH\cdot C_6H_4\cdot SMe$, prepared by boiling an alcoholic solution of the *p*-methylthiolaniline and 1-chloro-2 : 4-dinitrobenzene with potassium acetate, crystallises from glacial acetic acid in dark orange-red needles or stout plates, m. p. 141°, and when reduced with an aqueous alcoholic solution of sodium sulphide yields 4-*nitro*-2-*amino*-4′-*methylthioldiphenylamine*, $NO_2\cdot C_6H_3(NH_2)\cdot NH\cdot C_6H_4\cdot SMe$, which crystallises from alcohol in dark reddish-brown needles or plates, m. p. 128°. Its solution in concentrated sulphuric acid has a deep bluish-green colour.

The diazonium chloride from *p*-methylthiolaniline couples with an alkaline solution of β-naphthol, yielding a deep red *azo-dye*. The *diazoamino*-compound, $SMe\cdot C_6H_4\cdot N:N\cdot NH\cdot C_6H_4\cdot SMe$, crystallises from light petroleum in pale brown needles, m. p. 99°. p-*Methylthiolbenzonitrile*, $CN\cdot C_6H_4\cdot SMe$, crystallises from dilute methyl alcohol in colourless plates, m. p. 64°, and on hydrolysis yields p-*methylthiolbenzoic acid*, $SMe\cdot C_6H_4\cdot CO_2H$, which crystallises in colourless, flat needles, m. p. 192°. 1-*Methylthiol*-4-*iodobenzene*, $C_6H_4I\cdot SMe$, crystallises in colourless plates, m. p. 38°; the *dibromide*, $C_6H_4I\cdot SBr_2Me$, crystallises in dark garnet-red needles, and with water yields the *sulphoxide*, $C_6H_4I\cdot SOMe$, which crystallises from light petroleum in needles, m. p. 112°. The *iododichloride*, $ICl_2\cdot C_6H_4\cdot S\cdot CCl_3$, prepared by the action of chlorine on a chloroform solution of the iodo-derivative in the absence of all traces of moisture, crystallises in pale yellow needles, and by the removal of chlorine yields p-*iodophenyl trichloromethyl sulphide*, $C_6H_4I\cdot S\cdot CCl_3$, which crystallises from light petroleum in colourless needles, m. p. 103°. Aniline reacts with the trichloro-derivative, yielding triphenylguanidine and *iodophenyl mercaptan*, $C_6H_4I\cdot SH$, the latter of which crystallises in nacreous plates, m. p. 85°. Other

methylthiols react in a similar manner. p-*Nitrophenyl trichloromethyl sulphide*, $NO_2\cdot C_6H_4\cdot S\cdot CCl_3$, has m. p. 94°. *Acetylaminochlorophenyl trichloromethyl sulphide*, $NHAc\cdot C_6H_3Cl\cdot S\cdot CCl_3$, crystallises in plates, m. p. 136°. It reacts with aniline, yielding triphenylguanidine and acetylaminochlorophenyl mercaptan, the *disulphide* of which has m. p. 181°.

When the *p*-iodophenyl methyl sulphide is treated with chlorine in chloroform solution, and then exposed to the air and shaken with potassium iodide solution, Langmuir's *p*-iodobenzenesulphonyl chloride (Abstr., 1895, i, 230) is obtained. The corresponding *anilide*, $C_{12}H_{10}O_2NSI$, forms colourless, fibrous needles, m. p. 143°.

J. J. S.

Action of Bromine on Diphenyl Sulphide, Diphenyl Sulphoxide, and Diphenylsulphone. JACOB BÖESEKEN (*Rec. trav. chim.*, 1910, **29**, 315—329).—Bromine reacts with diphenyl sulphide to give a mixture of 4-bromodiphenyl sulphide and 4 : 4′-dibromodiphenyl sulphide. With chlorine in glacial acetic acid solution, 4 : 4′-dichlorodiphenyl sulphide is produced, but with dilute acetic acid only the sulphone. In the case of diphenylsulphoxide, a direct replacement by bromine does not take place, but in the presence of a little hydrobromic acid, 4 : 4′-dibromodiphenyl sulphide is formed, as in the case of the sulphide; no corresponding chloro-derivative is produced by the action of chlorine. Bromine does not react easily with diphenylsulphone, but at high temperatures the molecule is broken up with the formation of sulphuryl bromide and bromobenzene; a similar change is brought about by the action of chlorine.

N. C.

Electrolytic Oxidation of Aromatic Sulphides. FRITZ FICHTER and PH. SJÖSTEDT (*Ber.*, 1910, **43**, 3422—3429).—The electrolytic oxidation of benzyl sulphide gives three different products according to the conditions. In all cases the benzyl sulphide is dissolved in glacial acetic acid and a platinum anode used; a divided cell is unnecessary, since the products of reaction are only reduced with difficulty at a platinum cathode. If concentrated hydrochloric acid is added to the glacial acetic acid solution, and electrolysis carried out at 25°, using 0·08 ampere per sq. cm., and passing slightly less than the theoretical current, an almost theoretical yield of benzyl sulphoxide is obtained. Excess of current should be avoided, or else benzaldehyde is formed. Benzyl sulphide dichloride is probably first formed, and this is then hydrolysed into benzylsulphoxide and hydrogen chloride. Oxygen acids in place of hydrochloric acid give rise to further oxidation products of benzyl sulphide.

When the oxidation is carried out in hydrochloric-acetic acid solution at 90—95°, benzyldisulphoxide is formed. The benzylsulphoxide first formed is decomposed by the hydrochloric acid, the chief product being benzyldisulphide (compare Smythe, Trans., 1909, **95**, 349); the benzyl disulphide is then oxidised to the disulphoxide. Special experiments proved that benzyldisulphoxide is readily obtained by the electrolytic oxidation of benzyl disulphide.

When sulphuric acid is added to the acetic acid instead of hydrochloric acid, and the electrolysis carried out at 18°, *tribenzylsulphinium sulphate*, $(C_7H_7)_3S\cdot SO_4H$, is formed. The benzyl sulphide is oxidised to a mixture of benzyl alcohol and benzylsulphinic acid,

$$(C_7H_7)_2S + 2O + H_2O = C_7H_7\cdot OH + C_7H_7\cdot SO_2H,$$

and the former compound, in the presence of sulphuric acid, unites with the excess of benzyl sulphide, forming tribenzylsulphinium sulphate. This is proved by the ready formation of this compound by the interaction of benzyl sulphide and benzyl alcohol in sulphuric-glacial acetic acid solution at 70°. It is also formed by dissolving mono-tribenzylsulphinium ferrichloride in water, precipitation of the iron with ammonium hydroxide, and addition of ammonium sulphate and excess of sulphuric acid to the filtrate.

Tribenzylsulphinium sulphate forms cubes from alcohol, m. p. 170—175° (decomp.).

Replacement of hydrochloric and sulphuric acids by hydrobromic, hydrofluoric, nitric or phosphoric acids, addition of cerium salts as oxygen carriers, etc., did not give such good results in the electrolytic oxidation.

Dibenzylsulphone could not be prepared electrolytically either from benzyl sulphide or sulphoxide, but diphenylsulphone is readily obtained from phenyl sulphide at 20—30° in hydrochloric-glacial acetic acid solution. Diphenylsulphoxide prepared electrolytically is always mixed with unchanged phenyl sulphide and with diphenylsulphone. T. S. P.

Transformations of *cyclo*Butyldimethylcarbinol. IV. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1211—1227. Compare Abstr., 1908, i, 530, 864).—*cyclo*Butyldimethylcarbinol reacts with oxalic acid, yielding *cyclo*pentane derivatives and a crystalline isomeric alcohol of higher b. p., 1 : 1-*dimethyl*cyclo*pentan-2-ol*, $\begin{matrix}CH_2\cdot CMe_2\\ | \\ CH_2 - CH_2\end{matrix}\!\!>\!CH\cdot OH$, which, when oxidised with potassium permanganate or chromic acid, yields the corresponding pentanone (the semicarbazone of which has m. p. 191°) and $\alpha\alpha$-dimethylglutaric acid. 1 : 1-Dimethyl*cyclo*pentan-2-one,

$$\begin{matrix}CH_2\cdot CH_2\\ | \\ CH_2 - CO\end{matrix}\!\!>\!CMe_2,$$

has b. p. 143—143·5°/752 mm., D_0^{20} 0·8988, n_D^{20} 1·4343, and always gives some aldehydic reactions. When oxidised with potassium permanganate it yields: (1) *as*-dimethylsuccinic acid; (2) $\alpha\alpha$-dimethylglutaric acid, hexagonal plates, m. p. 83·5—84°, of which the *silver* salt, $C_7H_{10}O_4Ag_2$, and *aniline* salt, m. p. 144·5°, were prepared. The latter when boiled yields *dimethylglutaranil*, $CH_2\!<\!\begin{matrix}CMe_2\cdot CO\\ CH_2 - CO\end{matrix}\!>\!NPh$, hexagonal plates, m. p. 122—122·5°.

When treated with hydrazine hydrate, 1 : 1-dimethyl*cyclo*-

pentanone yields an *hydrazone*, $\begin{matrix}CH_2\cdot CMe_2\\ | \\ CH_2-CH_2\end{matrix}\!\!>C\colon N\cdot NH_2$, m. p. 20—24°, b. p. 101—104°/30 mm., D_0^{20} 0·9368, n_D^{20} 1·4859 ; it reduces ammoniacal silver solution, and is readily decomposed by water. With magnesium methyl iodide, the pentanone yields 1 : 1 : 2-trimethyl*cyclo*pentan-2-ol, b. p. 80—81°/49 mm., 156°/755 mm., D_0^{20} 0·9102, n_D^{20} 1·4513, which forms a crystalline *hydrate*, $(C_8H_{16}O),2H_2O$, m. p. 59—60°. Blanc's compound (*Compt. rend.*, 1906, **142**, 105), obtained similarly, was a hydrate and not the free pentanol. When distilled with oxalic acid, the trimethylpentanol yields 1 : 1 : 2-trimethyl*cyclo*pentene (*iso*laurolene),

$$\begin{matrix}CH\colon CMe\\ | \\ CH_2\cdot CH_2\end{matrix}\!\!>CMe_2,$$

b. p. 108·5—109°/754 mm., D_0^{15} 0·7868, D_{15}^{15} 0·7871, D_0^0 0·7824, n_D^{20} 1·4324, which with ammoniacal silver oxide solution yields a silver mirror, and when reduced with hydrogen iodide forms 1 : 1 : 2-trimethyl*cyclo*pentane, b. p. 113—114°/749 mm., D_{15}^{15} 0·7706, D_0^{20} 0·7661, n_D^{20} 1·4199.

In the formation of 1 : 1-dimethylpentanone by the oxidation of the pentanol, a volatile *acid*, $C_6H_{11}\cdot CO_2H$, is formed as a by-product ; the *silver* salt was prepared. Z. K.

Diphenyl*cyclo*butylcarbinol and its Transformations. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1227—1236).—Diphenyl*cyclo*butylcarbinol, $CH_2<\begin{matrix}CH_2\\ CH_2\end{matrix}>CH\cdot CPh_2\cdot OH$, is obtained by the action of *cyclo*butanecarboxylic acid on magnesium phenyl iodide, diphenyl being found as a by-product. It forms regular, rhombohedral crystals, m. p. 54—54·5°, b. p. 198°/13 mm., D_0^{20} 1·0906, n_D^{20} 1·5882, and with hydrogen bromide yields a *bromide*, $C_{17}H_{17}Br$, m. p. 94·5—95°. When boiled with oxalic acid, it forms *diphenyl*cyclo*butylidenemethane*, $CH_2<\begin{matrix}CH_2\\ CH_2\end{matrix}>C\colon CPh_2$, m. p. 58°, which with chromic acid mixture is oxidised to benzophenone, whilst with nitric acid the unsaturated hydrocarbon decomposes into benzophenone and succinic acid. It dissolves in a saturated solution of hydrogen bromide in glacial acetic acid, forming a *bromide*, seemingly identical with the one obtained from diphenyl*cyclo*butylcarbinol, but with bromine in carbon disulphide solution, it forms a *dibromide*, $CH_2<\begin{matrix}CH_2\\ CH_2\end{matrix}>CBr\cdot CPh_2Br$, m. p. 91—92°, which when boiled with methyl alcohol forms *diphenylbromo*cyclo*butylcarbinyl methyl ether*, $CH_2<\begin{matrix}CH_2\\ CH_2\end{matrix}>CBr\cdot CPh_2\cdot OMe$, m. p. 81—81·5°. When reduced with sodium ethoxide, diphenyl*cyclo*butylidenemethane forms either elongated plates or stout, hexagonal crystals of *diphenyl*cyclo*butylmethane*, $CH_2<\begin{matrix}CH_2\\ CH_2\end{matrix}>CH\cdot CHPh_2$, m. p. 39·5°, $D_4^{43\cdot5}$ 1·0003, $n_D^{43\cdot5}$ 1·5636, which is very stable, but dissolves in fuming nitric acid, D 1·52, yielding *dinitrodiphenyl*cyclo*butylmethane*, $C_4H_7\cdot CH(C_6H_4\cdot NO_2)_2$, m. p. 179°, whilst when boiled with nitric acid,

D 1·4, benzophenone and succinic acid are produced. When reduced with hydrogen iodide, diphenyl*cyclo*butylidenemethane forms a *hydrocarbon*, $C_{17}H_{18}$, m. p. 65°, isomeric with diphenyl*cyclo*butylmethane.
Z. K.

Production of β-Benzopinacolin. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1236—1237).—β-Benzopinacolin is most conveniently prepared by heating benzophenone with tin and fuming hydrochloric acid on the water-bath for about an hour, stirring the mixture from time to time. The mixture is then diluted with water, filtered, and the β-benzopinacolin is freed from tin by solution in boiling ethyl acetate, from which it crystallises in slender, colourless needles, m. p. 182·5°.
Z. K.

A Method of Isolating Cholesterol and Cerebrosides from Brain by means of Saponification with Barium Hydroxide in Methyl Alcohol. J. LORRAIN SMITH and W. MAIR (*J. Path. Bact.*, 1910, **15**, 122).—Brain is hardened in formaldehyde, cut into slices, and dried. It is then pounded in a mortar, and extracted with chloroform in a Soxhlet apparatus. The chloroform is evaporated off, and the dry extract dissolved in methyl alcohol. A hot saturated solution of barium hydroxide in methyl alcohol is added, and the whole boiled with a reflux condenser for three hours. After cooling, the reaction should be alkaline. It is made nearly neutral by acetic acid, and evaporated to dryness. The residue is placed in a Soxhlet thimble, which is suspended in a wide-necked flask under a reflux condenser, and over acetone kept boiling on a water-bath. As cerebrosides are comparatively insoluble even in boiling acetone, a white precipitate soon appears. After six hours, the acetone contains practically all the cholesterol and most of the cerebrosides. The extraction is repeated with a fresh supply of acetone. The cerebrosides settle out on cooling the acetone; the cholesterol remains in solution. Lecithin and ordinary fats are by this method converted into insoluble barium soaps.
W. D. H.

The Effect of Glycerol on the Clearing Point of Cholesterol and Cerebrosides. J. LORRAIN SMITH and W. MAIR (*J. Path. Bact.*, 1910, **15**, 122—123).—The clearing point of cholesterol (examined on the hot stage of a polarising microscope) is raised 5° by the presence of glycerol; that of cholesterol acetate is unaffected; the glycerol-cholesterol compound, if one exists, is easily decomposed by water, for, after the addition of water, cholesterol crystallises out unchanged.

On heating the white powder obtained by acetone from brain tissue, this substance (a cerebroside) assumes at 80° a fluid crystalline condition, and somewhat over 200° it clears sharply, showing only slight signs of decomposition; this corresponds with the melting point of other observers. When tested in glycerol, "myelin figures" appear at 100° and clear at 160°. When heated in water at comparatively low temperatures, the cerebroside gives myelin figures which are doubly refracting.
W. D. H.

Phytosterol and Cholesterol. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1910, **69**, 473—475).—A discussion of the views of the author and of others on the relationships of cholesterol and the phytosterols. W. D. H.

Compounds of Aluminium Chloride and Bromide with Acid Chlorides. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1310—1318. Compare Perrier, Abstr., 1903, i, 578).—Aluminium chloride forms a crystalline compound with benzoyl chloride, $AlCl_3,BzCl$, m. p. 93°. The concentration-temperature curve consists of three branches, with a eutectic point at $-7·5°$ at the composition $AlCl_3,6·53BzCl$. When the mixture contains 61% aluminium chloride, viscid, resinous, vaselin-like substances are formed, which crystallise with great difficulty. Aluminium bromide yields a similar crystalline, molecular compound, $AlBr_3,BzCl$, m. p. 90°. The curve has two eutectic points, at $-5°$ and composition $AlBr_3,6·66BzCl$, and at 7—8° at about the composition $AlBr_3,0·54BzCl$.

Aluminium halides behave towards organic acids as they do to alcohols and water, yielding halogen acid with development of much heat. Z. K.

Esters of *p*-Aminobenzoic Acid. ALFRED EINHORN and RUDOLF SEUFFERT (*Ber.*, 1910, **43**, 2995—3001).—The physiological value of diethylaminoethyl *p*-aminobenzoate has made it desirable to study other basic esters of *p*-aminobenzoic acid.

On heating chloroacetamide with ethyl *p*-aminobenzoate in presence of potassium iodide and sodium acetate, *ethyl* 2 : 5-*diketopiperazine*-1 : 4-*dibenzoate*, $CO_2Et·C_6H_4·N<\genfrac{}{}{0pt}{}{CH_2·CO}{CO·CH_2}>N·C_6H_4·CO_2Et$, crystallising in rhombic prisms, m. p. 217—218°, is formed. From the mother liquors, the *glycinamide* of *ethyl* p-*aminobenzoate*, $CO_2Et·C_6H_4·NH·CH_2·CO·NH_2$, is obtained in long, thin needles, m. p. 142°.

When boiled with formaldehyde and diethylamine in alcoholic solution, *ethyl* p-*carboxyphenylglycinediethylaminomethylamide*,

$$CO_2Et·C_6H_4·NH·CH_2·CO·NH·CH_2·NEt_2,$$

is formed, crystallising in indefinite prisms, m. p. 97—98°.

With formaldehyde and piperidine, *ethyl* p-*carboxyphenylglycine-piperidinomethylamide*, $CO_2Et·C_6H_4·NH·CH_2·CO·NH·CH_2·C_5NH_{10}$, results; it crystallises in colourless needles, m. p. 102°. The *hydrochloride* crystallises in needles, m. p. 154°; the *hydrobromide* forms prisms, m. p. 162°.

On boiling an alcoholic solution of sodium *p*-nitrobenzoate, chloroacetamide and sodium iodide, p-*nitrobenzoyloxyacetamide*,

$$NO_2·C_6H_4·CO·O·CH_2·CO·NH_2,$$

is formed in needles, m. p. 171—172°. When heated with formaldehyde and diethylamine, ethyl *p*-nitrobenzoate is obtained. On reduction, *p*-aminobenzoyloxyacetamide results in the form of needles, m. p. 159—160°.

Ethyl p-*nitrobenzoyloxyacetate*, $NO_2·C_6H_4·CO·O·CH_2·CO_2Et$, prepared by the interaction of sodium nitrobenzoate and ethyl chloroacetate, forms colourless needles, m. p. 39—40°. *Ethyl* p-*aminobenzoyl*-

oxyacetate crystallises in prismatic needles, m. p. 84°. p-*Carboxy*-p-*phenylglycinamide*, $CO_2H\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, prepared from sodium *p*-aminobenzoate, chloroacetamide and sodium iodide, forms prisms, m. p. 251°. E. F. A.

Some Derivatives of *p*-Aminobenzonitrile. MARSTON T. BOGERT and LOUIS ELSBERG WISE (*J. Amer. Chem. Soc.*, 1910, 32, 11, 1494—1499. Compare Bogert and Kohnstamm, Abstr., 1903, i, 559). —Improved methods are given for the preparation of *p*-nitro- and *p*-amino-benzonitriles, and some of their derivatives are described.

p-*Formylaminobenzonitrile* forms small, colourless crystals, m. p. 188—189° (corr.). A new method for the preparation of *p*-acetylaminobenzonitrile is given, which yields colourless needles, m. p. 205·5° (corr.). p-*Acetylaminobenzamide* crystallises in colourless prisms, m. p. 274·5°, with preliminary softening and sublimation. By the nitration of *p*-acetylaminobenzonitrile, 3-*nitro*-4-*acetylaminobenzonitrile* is obtained in long, yellow needles, m. p. 131·5° (corr.). p-*Benzoylaminobenzonitrile* melts at 170—170·5° (corr.); p-*benzenesulphonylaminobenzonitrile* forms colourless, arborescent crystals, m. p. 175—176° (corr.).

Methyl-p-*cyano-oxanilate*, $CO_2Me\cdot CO\cdot NH\cdot C_6H_4\cdot CN$, crystallises in leaflets, m. p. 208·5—209·5° (corr.); the *ethyl* derivative forms flat prisms, m. p. 188·5—189° (corr.). *Di*-p-*cyano-oxanilide*,

$$CN\cdot C_6H_4\cdot NH\cdot CO\cdot CO\cdot NH\cdot C_6H_4\cdot CN,$$

melts above 288°.

3 : 4-*Diaminobenzonitrile* crystallises in colourless needles, m. p. 147·5° (corr.). N. C.

Hydrogen Persulphide. V. Aldehydes and Hydrogen Persulphide. IGNAZ BLOCH, FRITZ HÖHN, and GÜNTHER BUGGE (*J. pr. Chem.*, 1910, [ii], 82, 473—485. Compare Abstr., 1908, ii, 579).—When benzaldehyde and crude hydrogen persulphide interact in the presence of zinc chloride or hydrogen chloride, the mixture becomes warm and a brown resin is gradually deposited, which becomes solid on pouring into water. On shaking this resin with alcoholic potassium hydroxide, phenylcarbithionic acid (dithiobenzoic acid), $C_6H_5\cdot CS_2H$ (compare Abstr., 1906, i, 847), is formed, and can be readily isolated (see succeeding abstract). A similar reaction takes place with other aldehydes, salicylaldehyde giving *o-hydroxyphenylcarbithionic acid* (*dithiosalicylic acid*), $HO\cdot C_6H_4\cdot CS_2H$, and anisaldehyde yielding p-*methoxyphenylcarbithionic acid* (*dithioanisic acid*), $OMe\cdot C_6H_4\cdot CS_2H$. The two latter acids are crystalline and intensely coloured, whereas phenylcarbithionic acid is a violet oil. They are all unstable in the air, undergoing rapid oxidation with the formation of resins. The salts of the heavy metals are coloured and comparatively easily soluble in organic solvents, some of them being soluble in ether.

On gentle oxidation, the dithio-acids give rise to thioacyldisulphides. Methyl and ethyl esters can also be obtained.

In the preparation of these carbithionic acids it is immaterial whether crude hydrogen persulphide or pure hydrogen disulphide or trisulphide is used.

In the absence of a condensing agent the reaction proceeds differently.

If benzaldehyde is gradually added to cooled hydrogen disulphide, the liquid becomes brown, and after a time a white precipitate of an additive compound of 2 molecules of benzaldehyde with 1 molecule of hydrogen disulphide is formed. A similar compound results when hydrogen disulphide is replaced by hydrogen trisulphide. Anisaldehyde, cinnamaldehyde, and salicylaldehyde react similarly (compare Abstr., 1908, i, 900).

These compounds are white, well crystallised, and possess a more or less irritating odour. They are comparatively unstable, but the benzaldehyde compound with hydrogen disulphide may be preserved for months. The disulphide are more stable than the trisulphide compounds. On treatment with ice-cold hydrochloric acid they are split up into their components; alcoholic potassium hydroxide gives potassium polysulphides and the reaction products of the aldehyde with alkali. On recrystallising the trisulphide compounds from carbon disulphide, there is a tendency for sulphur to be lost, with the formation of the disulphide compounds.

From the analogy of hydrogen persulphide to hydrogen peroxide, the above additive compounds are considered to be *dibenzylidene disulphide hydroxide* and *dibenzylidene trisulphide hydroxide*, with the formulæ: OH·CHPh·S·S·CHPh·OH and

OH·CHPh·S·S·S·CHPh·OH

respectively (compare dibenzylidene peroxide hydroxide,

OH·CHPh·O·O·CHPh·OH).

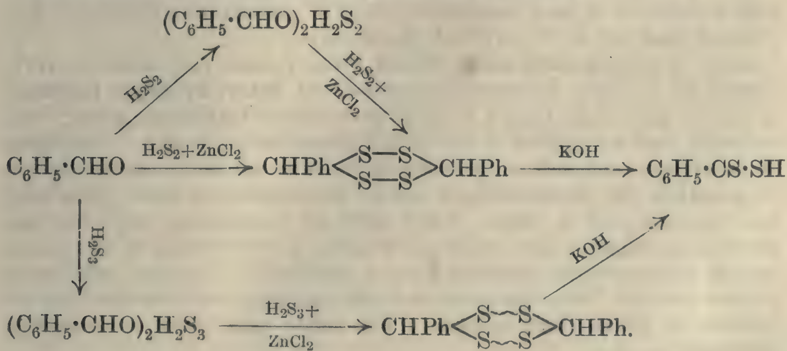
It is possible that the resinous intermediate product formed by the interaction of aldehydes and hydrogen persulphide in the presence of condensing agents is *dibenzylidene tetrasulphide*,

$$\mathrm{CHPh}{<}\begin{matrix}\mathrm{S\cdot S}\\ \mathrm{S\cdot S}\end{matrix}{>}\mathrm{CHPh},$$

corresponding with dibenzylidene peroxide, $\mathrm{CHPh}{<}\begin{matrix}\mathrm{O\cdot O}\\ \mathrm{O\cdot O}\end{matrix}{>}\mathrm{CHPh}$.

This is supported by the fact that the analytical results agree approximately with the formula $C_{14}H_{12}S_4$; also, when dibenzylidene disulphide hydroxide is heated with zinc chloride or shaken with zinc chloride and hydrogen persulphide in the cold, the resinous intermediate product is formed, from which phenylcarbithionic acid is readily obtained.

The results obtained can be represented as follows:



Cinnamaldehyde behaves somewhat differently from the other aldehydes towards hydrogen persulphide. The methyl ester obtained from the resinous intermediate product contains two S-atoms in excess of that required by dithiocinnamic acid, and reacts with bromine without evolution of hydrogen bromide. The formula assigned to this ester is CSPh·CS·CS·SMe. Styrene also adds on sulphur, but the resulting compound will not further unite with bromine; thus hydrogen persulphide can be used to add on sulphur to unsaturated linkings. It behaves as a strong vulcanising agent towards rubber. T. S. P.

Dithio-acids (Carbithionic Acids). FRITZ HÖHN and IGNAZ BLOCH (*J. pr. Chem.*, 1910, [ii], **82**, 486—511).—To a solution of crude hydrogen persulphide in benzene are added zinc chloride and benzaldehyde, shaking and cooling meanwhile. After twelve hours, the reaction mixture is heated on the water-bath, and finally treated with steam for three hours, after which time an orange-brown resin is formed, which, on pouring in water, solidifies to a vitreous, amorphous mass. A purer product is obtained by using pure hydrogen disulphide and hydrogen chloride as the condensing agent. It could not be obtained crystalline, although it is readily soluble in carbon disulphide; it has m. p. 80—90°, and decomposes at 120°. The analytical figures agree approximately with the formula $C_{14}H_{12}S_4$. To prepare phenylcarbithionic acid from this substance, it is shaken for two hours with a saturated alcoholic solution of potassium hydroxide, and the resulting brownish-red solution, after filtering from insoluble matter, treated in one of the two following ways: (1) carbon dioxide is passed into the solution, and, after collecting the precipitated potassium hydrogen and potassium ethyl carbonates, the greater part of the alcohol is expelled from the filtrate, which is then diluted with water. Lead acetate is carefully added to the solution until the lead sulphide precipitate first formed is succeeded by a red precipitate of lead phenylcarbithionate. The lead sulphide is then collected, and excess of lead acetate added to the filtrate to precipitate all the phenylcarbithionic acid. (2). The greater part of the alcohol is expelled from the solution, and the hydrogen persulphide destroyed with sulphurous acid. The phenylcarbithionic acid is then precipitated as an oil with hydrochloric acid, dissolved in benzene, and the lead salt formed by shaking the benzene solution with a solution of lead acetate in excess of potassium hydroxide. The yield of lead salt is 70—75% of the theory.

Lead phenylcarbithionate, $Pb(CS_2Ph)_2$, forms red needles from xylene, m. p. 200°. It is not decomposed by water, hydrogen sulphide, or dilute acids, but reacts readily with alkali sulphides, giving lead sulphide and a solution of the alkali phenylcarbithionate. Solutions of *potassium* and *sodium phenylcarbithionate* are fairly stable, but on evaporation on the water-bath partial decomposition takes place with the formation of a resin. They give no precipitates with barium, strontium, calcium, and magnesium salts, but with salts of the heavy metals characteristic precipitates are produced. The *zinc* salt forms yellow needles from benzene, and the *mercury* salt brownish-yellow needles or plates from benzene. The *silver* salt forms an unstable, chocolate powder.

Phenylcarbithionic acid, $Ph\cdot CS_2H$, is obtained as a heavy, violet-coloured oil by the addition of hydrochloric acid to a solution of the potassium salt (compare Abstr., 1906, i, 847). The *methyl* ester, $Ph\cdot CS_2Me$, is readily obtained by the action of methyl sulphate on an alkaline solution of the potassium salt. It is a red oil with a peculiar disagreeable, although somewhat aromatic, odour, b. p. 154—157°/20 mm., 275—280°/760 mm. (decomp.); it oxidises in the air. The *ethyl* ester, $Ph\cdot CS_2Et$, is similar in properties to the methyl ester, and is obtained from silver phenylcarbithionate and ethyl iodide, b. p. 158—162°/13 mm., 165—168°/19 mm.

Salicylaldehyde was condensed with hydrogen persulphide in a similar manner to that described for benzaldehyde, hydrogen chloride being used as the condensing agent. From the condensation product, *lead* o-*hydroxyphenylcarbithionate*, $Pb(S_2C\cdot C_6H_4\cdot OH)_2$, was obtained as orange-yellow needles. It is much less stable than lead phenylcarbithionate, and undergoes decomposition on recrystallisation (from benzene or xylene); it is decomposed on warming with water. It was necessary to estimate the sulphur by decomposing the compound in a current of chlorine, using Schaefer's apparatus (Abstr., 1906, ii, 394). A solution of the *potassium* salt is obtained by treating the lead salt with a solution of potassium sulphide. It gives characteristic precipitates with salts of the heavy metals; the *mercury* salt forms bright yellow, microscopic needles.

o-*Hydroxyphenylcarbithionic acid*, $OH\cdot C_6H_4\cdot CS_2H$, obtained from the solution of the potassium salt by the addition of hydrochloric acid, forms orange-yellow needles from light petroleum, m. p. 48—50°, and slowly oxidises in the air. On treating the solution of the potassium salt with methyl sulphate, a mixture of *methyl* o-*hydroxyphenylcarbithionate*, $OH\cdot C_6H_4\cdot CS_2Me$, and *methyl* o-*methoxyphenylcarbithionate*,

$$OMe\cdot C_6H_4\cdot CS_2Me,$$

is obtained. The former forms yellow needles, m. p. 10—20°, and the latter orange-yellow lamellæ, m. p. 43—44°. *Ethyl* o-*hydroxyphenylcarbithionate*, $OH\cdot C_6H_4,CS_2Et$, obtained from the silver salt and ethyl iodide, is an orange-yellow oil.

Oxidation of *o*-hydroxyphenylcarbithionic acid by leading air through the solution gives o-*hydroxythiobenzoyl disulphide*,

$$(OH\cdot C_6H_4\cdot CS)_2S_2;$$

brown leaflets from chloroform, m. p. 125—126°, to a blood-red liquid. A better yield (60%) is obtained by adding finely powdered sulphur to a methyl-alcoholic solution of the acid, hydrogen sulphide being evolved. Oxidation of the sodium salt of the acid with iodine or potassium ferricyanide is not a satisfactory method for preparing the disulphide. The *acetyl* derivative of the disulphide is obtained by acetylation with acetyl chloride in pyridine-glacial acetic acid solution; rose-colored powder, sinters at 74°, but only melts completely above 100°.

Lead p-*methoxyphenylcarbithionate*, $(OMe\cdot C_6H_4\cdot CS_2)_2Pb$, is obtained from the condensation product of anisaldehyde with hydrogen persulphide as a dark reddish-brown powder. It can be recrystallised without decomposition, and forms orange-yellow needles from benzene. The reaction with potassium sulphide is a reversible one. To prepare

the *potassium* salt, the free acid, obtained directly from the resinous condensation product by treatment with alcoholic potassium hydroxide and precipitation with hydrochloric acid, is dissolved in potassium hydroxide; it forms pale brownish-red needles. p-*Methoxyphenylcarbithionic acid*, $OMe\cdot C_6H_4\cdot CS_2H$, can be obtained as pale brownish-red crystals from light petroleum, but it is so unstable that it could not be prepared pure. A solution of the sodium or potassium salt gives characteristic precipitates with salts of the heavy metals; the *bismuth*, *zinc*, and *mercury* salts are crystalline. By oxidation of the potassium salt with iodine, a precipitate of p-*methoxythiobenzoyl disulphide*,

$$(OMe\cdot C_6H_4\cdot CS)_2S_2,$$

is obtained; m. p. 161—163°. *Methyl* p-*methoxyphenylcarbithionate* forms salmon-pink leaflets from methyl alcohol; m. p. 31° to a blood-red liquid. The *ethyl* ester forms yellow-orange needles, m. p. 25—26° to a red liquid.

A pure lead salt could not be obtained from the condensation product of cinnamaldehyde with hydrogen persulphide. By treating the condensation product directly with methyl sulphate, a substance was obtained possessing the formula $C_{10}H_8S_4$; orange-brown needles from methyl alcohol, m. p. 98—99° to a red liquid. The substance may probably be $CPhS\cdot CS\cdot CS_2Me$.

Pure hydrogen di- or tri-sulphide reacts with styrene, forming an almost colourless oil, with a very unpleasant odour. Phenanthrene and stilbene do not react with the pure hydrogen persulphides, whereas the latter are decomposed by linalool and geraniol. T. S. P.

Aminomethylbenzoic Acids [Aminotoluic Acids]. HENRY L. WHEELER and CHARLES HOFFMAN (*Amer. Chem. J.*, 1910, **44**, 507—508).—The acid obtained as the chief product of the nitration of *m*-toluic acid is not 4-nitro-*m*-toluic acid, as stated in an earlier paper (Abstr., 1910, i, 666), but is the 2-nitro-derivative, as was originally recorded by Jacobsen (Abstr., 1882, 185), and confirmed later by Findeklee (Abstr., 1906, i, 21) and Müller (Abstr., 1909, i, 160). The supposed derivatives of 4-amino-*m*-toluic acid described by the authors (*loc. cit.*) are therefore derivatives of 2-amino-*m*-toluic acid. E. G.

Ethyl Diazoacetate and *p*-Xylene. EDUARD BUCHNER and PAUL SCHULZE (*Annalen*, 1910, **377**, 259—284).—Ethyl diazoacetate reacts with *p*-xylene in much the same manner as with toluene (Buchner and Feldmann, Abstr., 1904, i, 57) and *m*-xylene (Buchner and Delbrück, *ibid.*, 1908, i, 87). Among the products is an ethyl dimethylnorcaradienenecarboxylate, which must be represented by one of the two formulæ:

$$\begin{matrix} CH\!:\!CMe\cdot CH \\ | \qquad\quad | \\ CH\!:\!CMe\cdot CH \end{matrix}\!\!>\!CH\cdot CO_2Et \quad \text{or} \quad \begin{matrix} CMe\!:\!CH\cdot CH- \\ | \qquad\quad | \\ CH\!:\!CH-CMe \end{matrix}\!\!>\!CH\cdot CO_2Et.$$

The former of these is the more probable, as the ester is transformed readily into ethyl β-*p*-tolylpropionate, and, as in other cases, the $>CH\cdot CO_2Et$ group condenses with the carbon atoms of the hexa-ring, which are as far removed from the methyl substituents as possible. The condensation product is therefore *ethyl* 2 : 5-*dimethyl*-$\Delta^{2:4}$-*norcara-*

dienenecarboxylate. On distillation, a 53—55% yield of an oil, b. p. 128—136°/12 mm., is obtained, but this contains, in addition to the above ester, two isomeridic condensation products, namely, appreciable amounts of an ethyl *cyclo*heptatrienecarboxylate and small amounts of ethyl *β-p*-tolylpropionate. The separation of these compounds is best accomplished by means of ammonia, as in the three esters the carbethoxy-group is attached repectively to secondary, tertiary, and primary carbon atoms (compare E. Fischer and Dilthey, Abstr., 1902, i, 269). It is an advantage to use a mixture of the methyl esters, as they react more readily with the ammonia. The addition of copper powder as a catalyst in the condensation does not give any better yields, but leads to the formation of appreciable amounts of methyl fumarate, a compound which is not formed in the absence of the metal.

2 : 5-*Dimethyl*-$\Delta^{2:4}$-*norcaradiene*-7-*carboxylamide*, $C_{10}H_{13}ON$, obtained by shaking the mixture of methyl esters for two days with a solution of ammonia saturated at 0°, crystallises from ethyl alcohol in colourless needles, m. p. 163—164°. The yield is small, only about 0·4 gram from 10 grams of condensation product. *β-p*-Tolylpropionamide is also formed, but is much more readily soluble in concentrated ammonia solution. The unsaturated amide turns yellow on exposure to the air, reduces permanganate, and dissolves in concentrated sulphuric acid to a red solution. When boiled with dilute sulphuric acid, it yields *p*-xylylacetic acid (compare Guerbet, Abstr., 1898, i, 424), and when heated for five minutes with 5% sodium hydroxide solution, yields an acid, m. p. 98—99°, which is probably 2 : 5-*dimethyl*-$\Delta^{2:4:7}$-cyclo-*heptatriene*-7-*carboxylic acid*.

The isomeric 2:5-*dimethyl*-$\Delta^{7:2:5}$-cyclo*heptatriene*-7-*carboxylic acid*,

$$\begin{array}{l} CH_2\cdot CMe:CH \\ | \\ CH:CMe-CH \end{array}\!\!>\!C\cdot CO_2H,$$

is most readily obtained by heating the crude condensation product for ten hours at 160—170° in an evacuated sealed tube, then distilling under reduced pressure, and hydrolysing with 25% methyl-alcoholic potassium hydroxide, first at the ordinary temperature and then for thirty minutes on the water-bath. On the addition of sufficient sulphuric acid to precipitate 40% of the total acid present, the pure crystalline acid is obtained, and the addition of more sulphuric acid precipitates 10—12 grams of crystalline *β-p*-tolylpropionic acid (Kröber, Abstr., 1890, 969). The $\Delta^{2:5:7}$-acid is formed together with the tolylpropionic acid when the crude condensation product is heated with 15% sulphuric acid for fifteen to thirty hours, and may also be obtained by heating the amide of the dicyclic acid for five hours with water in an evacuated tube at 160—170°, and subsequent hydrolysis. When a temperature of 180—190° is used, the ammonium salt of the heptatriene acid is formed directly. The $\Delta^{2:5:7}$-acid, $C_{10}H_{12}O_2$, crystallises from 30% ethyl alcohol or 30% acetic acid in long, pale yellow, glistening needles, m. p. 136—137°. Its solution in concentrated sulphuric acid is yellow, but gradually turns reddish-brown. The calcium, copper, lead, iron, zinc, and silver salts are all very sparingly soluble. The *methyl* ester has b. p. 120—121°/12 mm.; the *amide*,

$C_{10}H_{13}ON$, crystallises from water in colourless needles, m. p. 136—137°; the *dibromide*, $C_{10}H_{12}O_2Br_2$, crystallises from light petroleum in colourless needles, m. p. 126° (decomp.), after changing colour at 110°, and the *tetrabromide*, $C_{10}H_{12}O_2Br_4$, has m. p. 185° (decomp.), after turning yellow at 160°.

2 : 5-*Dimethyl*-$\Delta^{2:5}$-cyclo*heptadiene-7-carboxylic acid*,

$$C_7H_7Me_2\cdot CO_2H,$$

prepared by reducing the heptatriene acid with 3% sodium amalgam in alkaline solution whilst carbon dioxide is passed through, has m. p. 38—40° in the crude state, and is too unstable to purify. The *amide*, $C_{10}H_{15}ON$, prepared from the chloride, crystallises from water in needles, m. p. 142°, and turns yellow on exposure to the air. The *dihydrobromide*, $C_{10}H_{16}O_2Br_2$, obtained by leaving the acid in contact with glacial acetic acid saturated with hydrogen bromide at 0°, crystallises from light petroleum in small needles, m. p. 120° (decomp.), and when boiled for three hours with sodium hydroxide solution yields 2 : 5-*dimethyl*-$\Delta^{2:6}$-cyclo*heptadiene-7-carboxylic acid*,

$$\begin{matrix} CH_2\cdot CHMe\cdot CH \\ | \\ CH\colon CMe-CH_2 \end{matrix}\!\!>\!C\cdot CO_2H,$$

which crystallises from dilute alcohol in colourless needles, m. p. 82°. The corresponding *amide* has m. p. 147—148°, and turns yellow on exposure to the air. 2 : 5-*Dimethyl*cyclo*heptane-7-carboxylic acid*,

$$C_7H_{11}Me_2\cdot CO_2H,$$

is formed when an ethereal solution of the $\Delta^{2:5:7}$-triene acid is reduced with hydrogen in the presence of finely divided platinum ; it is an oil which does not solidify when kept in a freezing mixture, and yields an *amide*, $C_{10}H_{19}ON$, which crystallises from 30% alcohol in glistening needles, m. p. 185—186°. 7-*Bromo*-2 : 5-*dimethyl*cyclo*heptane-7-carboxylic acid*, $C_7H_{10}Me_2Br\cdot CO_2H$, prepared by the Volhard-Zelinsky method, crystallises from concentrated formic acid in stout, colourless needles, m. p. 152—153°, after softening at 120°.

β-p-*Tolylpropionamide*, $C_6H_4Me\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2$, crystallises from hot water or ether in flat needles, m. p. 135°. The corresponding acid does not readily decolorise permanganate, and is oxidised by alkaline permanganate to terephthalic acid.

The conversion of the bicyclic condensation product into *p*-xylylacetic acid is represented as taking place by the addition and subsequent elimination of water, the intermediate hypothetical product being $\begin{matrix} CH\colon CMe\cdot CH\cdot OH \\ | \qquad\quad | \\ CH\colon CMe\cdot CH\cdot CH_2\cdot CO_2H \end{matrix}$. Similarly, with the conversion of the condensation product into β-*p*-tolylpropionic acid, a hypothetical intermediate product, formed by the addition of water, is assumed, namely, $CH(OH)_2\cdot CMe\colon CH\cdot CH\colon CMe\cdot CH_2\cdot CH_2\cdot CO_2H$.

The constitution of the 2 : 5-dimethyl-$\Delta^{2:5:7}$-*cyclo*heptatriene-7-carboxylic acid is discussed in detail. J. J. S.

Preparation of Substituted Cinnamic Acids. THEODOR POSNER (*J. pr. Chem.*, 1910, [ii], 82, 425—440).—The paper contains a description of the preparation of a large number of substituted cinnamic acids and their esters. The esters of nuclear-substituted

cinnamic acids are obtained best by boiling the acids for six hours with methyl or ethyl alcohol containing 10% of concentrated sulphuric acid. The following new compounds are described: m-*aminocinnamic acid acetate*, $C_9H_9O_2N,C_2H_4O_2$, is precipitated when acetic acid is added to the ammoniacal filtrate obtained after the reduction of *m*-nitrocinnamic acid by ferrous sulphate and ammonium hydroxide; it forms yellow crystals, m. p. 267° (decomp.). o-*Acetylaminocinnamic acid*, $NHAc\cdot C_6H_4\cdot CH\colon CH\cdot CO_2H$, m. p. 250—251°, is prepared from the acid and acetic anhydride. *Ethyl* o-*hydroxycinnamate*, m. p. 85—86°, is prepared by boiling *o*-coumaric acid with 2% alcoholic hydrogen chloride for six hours. *Methyl* p-*hydroxycinnamate* has m. p. 139—140°. *a*-*o*-Methoxycinnamic acid and its methyl ester are more conveniently obtained by methyl sulphate in the cold than by Perkin's method with methyl iodide at 150° (Trans., 1877, 39, 418). *β*-*o*-Methoxycinnamic acid is most conveniently obtained by boiling salicylaldehyde methyl ether (prepared from salicylaldehyde, aqueous sodium hydroxide, and methyl sulphate), sodium acetate, and acetic anhydride for nine hours. *m*-Methoxycinnamic acid is best prepared, although in only moderate yield, from *m*-methoxybenzaldehyde and malonic acid by Knoevenagel's method; its *methyl* ester has b. p. 305—307°/748 mm. The esterification of 3 : 4-dihydroxycinnamic acid by methyl alcohol and sulphuric acid yields anomalous results, the products being a *substance*, $C_{11}H_{12}O_4$, m. p. 131—132°, which is insoluble in sodium carbonate, and another *substance*, $C_{10}H_{10}O_4$, m. p. 159—160°, which is soluble in sodium carbonate and is reprecipitated by sulphuric acid. *Methyl* 3 : 4-*methylenedioxycinnamate* has m. p. 133—134°. *Ethyl β-phenyl-a-methylacrylate*, $CHPh\colon CMe\cdot CO_2Et$, conveniently prepared from ethyl propionate, sodium, and benzaldehyde in the cold, has b. p. 220—230°. *Methyl β-phenyl-a-ethylacrylate*, $CHPh\colon CEt\cdot CO_2Et$ b. p. 250—260°, is obtained in a similar manner from ethyl butyrate. *Methyl ββ-diphenylacrylate* has b. p. 194·6—194·8°/13 mm. C. S.

Crystallisation of Sodium Salicylate Solution. CHARLES A. HILL (*Pharm. J.*, 1910, [IV], 31, 730—731).—Solutions of sodium salicylate, made by dissolving the commercial salt in its own weight of water, sometimes deposit spontaneously at the ordinary temperature in winter large masses of transparent crystals. This crystallisation is rarely obtained even below 0° unless the cold solution is inoculated with a crystal. The author obtained these crystals as large, well-defined prisms, exhibiting fluorescence and passing under the influence of heat or pressure into the anhydrous salt; analysis shows them to have the composition $C_7H_5O_3Na,6H_2O$.

The author also shows that commercial sodium salicylate is anhydrous. N. C.

Acylated Salicylic Acid Anhydrides. ALFRED EINHORN and RUDOLF SEUFFERT (*Ber.*, 1910, 43, 2988—2995).—Acylated salicylic acids [*o*-acyloxybenzoic acids] are converted by the action of chlorocarboxylic acid alkyl esters in presence of pyridine into alkyl *o*-acyloxybenzoyl carbonates, and these, when warmed on the water-bath, form anhydrides. Other acid chlorides act similarly towards

o-acyloxybenzoic acids, yielding mixed anhydrides; these are decomposed on heating with the formation of the two simple anhydrides. The mixed anhydrides also slowly decompose at the ordinary temperature in contact with pyridine.

Ethyl o-*acetoxybenzoyl carbonate*, $OAc\cdot C_6H_4\cdot CO\cdot O\cdot CO\cdot OEt$, was obtained as a colourless, viscid oil. *Amyl* o-*acetoxybenzoyl carbonate* is a faintly yellow, viscid oil. The *valeryloxy-* and *benzoyloxy-ethyl* esters are likewise viscid oils. *Ethyl* o-*cinnamoyloxybenzoyl carbonate* crystallises in needles, m. p. 57°.

o-*Acetyloxybenzoic anhydride*, $(OAc\cdot C_6H_4\cdot CO)_2O$, crystallises in lustrous plates, m. p. 85°.

o-*Benzoyloxybenzoic anhydride*, $(OBz\cdot C_6H_4\cdot CO)_2O$, forms prismatic needles, m. p. 110—111°. o-*Cinnamoyloxybenzoic anhydride*,

$$(CHPh\!:\!CH\cdot CO\cdot O\cdot C_6H_4\cdot CO)_2O,$$

separates in refractive prisms, m. p. 129—130°.

Benzoic o-*acetyloxybenzoic anhydride*, $C_6H_4(OAc)\cdot CO\cdot O\cdot CO\cdot C_6H_5$, crystallises in needles, m. p. 75—76°. *Benzoic* o-*benzoyloxybenzoic anhydride* crystallises in rhombic plates, m. p. 74—75°. *Cinnamic* o-*cinnamoyloxybenzoic anhydride* forms needles, m. p. 78—79°.

E. F. A.

Derivatives of Camphoroxalic Acid. XIII. J. BISHOP TINGLE and S. J. BATES (*J. Amer. Chem. Soc.*, 1910, **32**, 11, 1499—1517. Compare Abstr., 1899, i, 444; 1900, i, 302; 1901, i, 632; 1905, i, 799; 1906, i, 902; 1908, i, 125, 126).—The authors have made a further study of the condensation products of camphoroxalic acid and amines, and the action of various reagents on them. The results confirm the view that the constitution of these compounds is given by the formula $C_8H_{14}<\begin{smallmatrix}C\!:\!CR\cdot NR^1R^2\\ |\\ CO\end{smallmatrix}$, where $R = H$ or CO_2H; R^1 and $R^2 = H$, alkyl or aryl.

A comparison between the compounds resulting from the condensation of camphoroxalic acid with thiosemicarbazide and with semicarbazide shows that in the former there is much less tendency to form cyclic derivatives.

Phenylcamphoformeneaminecarboxylic acid,

$$C_8H_{14}<\begin{smallmatrix}C\!:\!C(NHPh)\cdot CO_2H\\ |\\ CO\end{smallmatrix},$$

was prepared by the method of Bishop Tingle and A. Tingle, and the effect of bromine, chlorides of phosphorus, and oxidising agents observed. By the action of methyl sulphate, *methyl phenylcamphoformeneaminecarboxylate* is obtained as yellow crystals, m. p. 127°. *Methyl methoxycamphoroxalate*, $C_8H_{14}<\begin{smallmatrix}C\!:\!C(OMe)\cdot CO_2Me\\ |\\ CO\end{smallmatrix}$, is obtained as an oil by the action of methyl sulphate and sodium carbonate on methyl camphoroxalate.

Thiosemicarbazylcamphoformeneaminecarboxylic acid,

$$C_8H_{14}<\begin{smallmatrix}C\!:\!C(CO_2H)\cdot NH\cdot NH\cdot CS\cdot NH_2\\ |\\ CO\end{smallmatrix},$$

exists in two modifications, one melting at 148—149°, the other at

120—125°. By fusion it forms a *compound*, m. p. 170°. The *ethyl* ester of the acid forms white crystals, m. p. 150—151°. By the action of acetic anhydride on the acid, *thiosemicarbazylcamphoformeneaminecarboxylactimide*, $\begin{matrix}C_8H_{14}\\ | \\ CO\end{matrix}\!\!>C:C<\!\!\begin{matrix}CO-NH\\ NH\cdot NH\end{matrix}\!\!>CS$, is obtained as bright red crystals, m. p. 181—182°.

m-4-Xylidine m-4-xylidylcamphoformeneaminecarboxylate,

$$\begin{matrix}C_8H_{14}\\ | \\ CO\end{matrix}\!\!>C:C<\!\!\begin{matrix}CO_2\cdot NH_3\cdot C_6H_3Me_2\\ NH\cdot C_6H_3Me_2\end{matrix},$$

forms brown crystals, m. p. 93—94°; the *acid* crystallises in yellow crystals, m. p. 117—118°.

p-*Chlorophenylcamphoformeneaminecarboxylic acid* crystallises in yellow needles, m. p. 182—183°.

p-*Chlorophenylcamphoformeneamine*, $C_8H_{14}<\!\!\begin{matrix}C:CH\cdot NH\cdot C_6H_4Cl\\ | \\ CO\end{matrix}$, forms white crystals, m. p. 194—195°.

Dibenzylamine camphoroxalate has m. p. 135—136°.

Dibenzylamine phenylcamphoformeneaminecarboxylate,

$$C_8H_{14}<\!\!\begin{matrix}C:C(NHPh)\cdot CO_2\cdot NH_2(CH_2Ph)_2\\ | \\ CO\end{matrix},$$

forms white crystals, m. p. 185°. m-*Carboxyphenylcamphoformeneaminecarboxylic acid* crystallises in white crystals, m. p. 136—137°. By the action of heat on the acid, m-*carboxyphenylcamphoformeneamine*, $C_8H_{14}<\!\!\begin{matrix}C:CH\cdot NH\cdot C_6H_4\cdot CO_2H\\ | \\ CO\end{matrix}$, is obtained in long, yellow needles, m. p. 116—117°.

By the condensation of benzidine and camphoroxalic acid, a yellow substance, m. p. 208°, is produced, which is probably an inner ammonium salt, and has the constitution $\begin{matrix}C_8H_{14}\\ | \\ CO\end{matrix}\!\!>C:C<\!\!\begin{matrix}CO\cdot O\cdot NH_3\\ \qquad\quad | \\ NH-C_{12}H_8\end{matrix}$.

Benzidylcamphoformeneamine, $C_8H_{14}<\!\!\begin{matrix}C:CH\cdot NH\cdot C_{12}H_8\cdot NH_2\\ | \\ CO\end{matrix}$, melts at 317—318°. By the condensation of camphylamine and camphoroxalic acid, a small quantity of a white *sublimate*, m. p. 105°, is obtained. N. C.

Chemistry of Alcapton-urine (Homogentisic Acid and Certain of its Derivatives). Carl Th. Mörner (*Zeitsch. physiol. Chem.*, 1910, 69, 329—365).—Homogentisic acid in the presence of ammonia and air gives, not only the brown coloration described by earlier authorities, but, under suitable conditions, an intensely brilliant reddish-violet coloration. The conditions necessary for the production of the coloration are: (*a*) concentration of homogentisic acid 0·25 to 2%. With more dilute solutions, yellowish-brown, and with more concentrated solutions blackish-brown, colorations are obtained. (*b*) Concentration of the ammonia 1 to 4%. (*c*) Oxygen concentration. It is essential that the amount of oxygen absorbed per unit of time shall not be too large. This is accomplished by using comparatively narrow tubes; thus with 20 c.c. of liquid, the reaction was given when tubes of 0·75 to 2·0 cm.

diameter were used, but only brown or brownish-red colorations were obtained with tubes 3·0 to 5·0 cm. diameter. If the volume of liquid is large and the tube very narrow, the time required for the coloration to appear may be considerable. Moderately concentrated solutions of many substances, for example, ammonium sulphate or chloride (1/50 saturated), potassium chloride (1/4—1/3 saturated), potassium hydroxide (1%), aniline (1/2%), carbamide (8%), alcohol (20%), prevent the formation of the coloration. Glycerol, dextrose, and sucrose at concentrations of 20% have no effect, and sodium chloride or sulphate solutions up to 1/3 saturated do not interfere. It has been found possible to isolate small amounts of two distinct compounds from the reddish-purple solution. These are termed α- and *β-alcaptochromes*. The α-compound crystallises from hot water in thin, hexagonal plates, with a metallic lustre and green reflex, and when heated above 105° decomposes without melting or subliming. It is only sparingly soluble in most solvents; the solutions have a yellow colour and do not fluoresce. The orange-yellow pyridine solution, when diluted with water, turns blood- or cherry-red. The compound is acidic, and dissolves in dilute alkali solutions, yielding colorations which resemble methyl-violet solutions. Such solutions are readily decolorised by the addition of a solution of ferrous sulphate plus a tartrate, but the colour is restored on shaking with air. The solutions in sodium or potassium hydrogen carbonate have a somewhat more reddish colour, and this changes to yellow when carbon dioxide is passed in

The solution in ammonium hydroxide has a violet colour, and the colour can be detected with a dilution of 1 in 20 millions; it becomes more red when heated, but returns to the original colour as it cools. The *ammonium* salt has been isolated as a solid with a green, metallic lustre. The acid also dissolves in concentrated sulphuric or hydrochloric acids, but does not appear to yield salts with them. The constitution suggested for the α-alcaptochrome is that of a 4-*imino*-p-*benzoquinone-2-acetic acid*, $NH\colon C_6H_3O\cdot CH_2\cdot CO_2H$.

The following hydroxylic derivatives do not yield colorations when treated in the same manner as homogentisic acid. Catechol, resorcinol, β-resorcylic acid, phloroglucinol, pyrogallol, gallic acid, tannin, protocatechuic acid. Neither do quinol, quinhydrone, dianilinoquinol, quinol dimethyl ether, arbutin, or gentisic acid. Toluquinol, on the other hand, gives an intense reddish-violet solution with an orange fluorescence. The coloured substance has been isolated as a magma of reddish-brown, crystalline needles, which dissolve in alkalis, yielding solutions with a reddish-violet colour and orange fluorescence. The addition of acetic acid or carbon dioxide to such solutions precipitates the colouring matter.

Hydroxyquinol gives a bluish-violet-coloured non-fluorescent solution. The coloured compound has been isolated as an amorphous, violet-brown, flocculent mass, insoluble in most solvents.

The coloration described by Langstein and Meyer (*Arch. Klin. Med.*, 1903, **78**, 161) as characteristic of homogentisic acid lactone is quite different from the alcaptochrome reaction, and by means of the latter it is shown that ammonium hydroxide solutions do

not readily hydrolyse the lactone, whereas solutions of sodium hydroxide do.

It is shown that many aromatic derivatives containing free hydroxyl groups in positions 1 and 4 react with aniline in the presence of air, yielding coloured, crystalline compounds, which are insoluble in water, but dissolve in organic solvents, and also give characteristic colorations with concentrated sulphuric acid. The method of procedure consists in mixing an aqueous solution of the hydroxy-compound with sufficient saturated aqueous solution of aniline or one of its homologues, and exposing to the air for several weeks in shallow dishes. The amorphous precipitates are removed, washed with 1% potassium carbonate solution, then with water, and crystallised from glacial acetic acid.

Quinol yields 2 : 5-dianilo-*p*-benzoquinone with aniline, 2 : 5-*p*-toluidino-*p*-benzoquinone with p-toluidine,and 2:5-*m*-xylidino-*p*-benzoquinone with *m*-xylidine.

Homogentisic acid (or alcapton-urine) and aniline under the given conditions yield 3 : 6-*dianilino*-p-*benzoquinone*-3-*acetic acid*,

$$CH{<}{\substack{CO\cdot C(NHPh)\\ C(NHPh)\cdot CO}}{>}C\cdot CH_2\cdot CO_2H,$$

which crystallises from glacial acetic acid in brownish-violet prisms with a coppery lustre, m. p. 228°. With sulphuric acid it gives a majenta-red coloration, which changes rapidly to cherry-red. The corresponding p-*toluidino*-derivative, $C_{22}H_{20}O_4N_2$, forms dark reddish-brown crystals, m. p. 231°, and gives a pure blue coloration with concentrated sulphuric acid; the m-*xylidino*-derivative, $C_{24}H_{24}O_4N_2$, forms brownish-yellow crystals, m. p. 241°, and also gives a blue coloration with sulphuric acid.

Quinhydrone, homoquinol, hydroxyquinol, gentisic acid, and 3-methoxy-1-propyl-2 : 5-quinol also react with aniline and air in a similar manner.

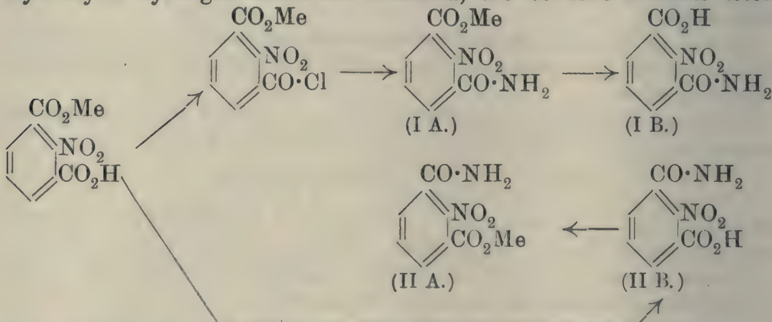
Homogentisic acid lactone acts very slowly with aniline and air, and then probably only as the result of hydrolysis; quinol dimethyl ether does not react.

The product described previously (Abstr., 1909, ii, 331) as obtained from normal urine, aniline, and air is also formed in the absence of urine if a small amount of a catalyst, for example, a ferrous salt, is present, and is regarded as dianilino-*p*-benzoquinonemonoanil. Its formation in the case of urine is due to the presence of small amounts of some catalyst, and not to the presence of quinol.

J. J. S.

Ester-acids and Amido-acids of the *iso*Phthalic Acid Series. The Question of Equivalence of Positions 2 and 6 in the Benzene Nucleus. Alfred Wohl (*Ber.*, 1910, 43, 3474—3489).—The non-existence of two isomeric ortho-disubstituted derivatives of benzene is usually explained at the present time by the assumption that the free affinities of the six nuclear carbon atoms are not arranged in three separate pairs of unsaturated systems, but are so distributed that they mutually neutralise one another. The isomerism of 1 : 2- and 1 : 6-derivatives,

if such are capable of existence, is due, not to the movements of a migratory atom or group as in typical cases of tautomerism, but to a difference in the distribution of the free affinities of the carbon atoms. Hitherto, all attempts to discover isomeric ortho-disubstituted benzene derivatives have depended on reactions which seek to introduce substituents directly into positions 2 or 6, that is, on reactions which interfere with the benzene nucleus itself, the natural result being that the free affinities of the nuclear carbon atoms become arranged in the position of greatest stability, and only one ortho-disubstituted derivative has been discovered. The author's method of attacking the problem is indicated by the annexed scheme; only the hydroxylic hydrogen atoms are attacked, the benzene nucleus itself



being uninterfered with. The substances I A and II A are found to be identical, not isomeric, and so also I B and II B. Similar results have been obtained with 2-hydroxy*iso*phthalic acid and with *iso*phthalic acid itself.

[With E. NAGELSCHMIDT.]—*Methyl hydrogen* iso*phthalate*,

$$CO_2H{\cdot}C_6H_4{\cdot}CO_2Me,$$

m. p. 193°, is obtained by boiling a methyl-alcoholic solution of methyl *iso*phthalate and one equivalent of sodium hydroxide for two to three hours, filtering any precipitated sodium salt, pouring the filtrate into water, extracting the unchanged ester with ether, and carefully acidifying the aqueous solution with hydrochloric acid; the first portion of the precipitate is almost pure methyl hydrogen *iso*phthalate. This is converted by thionyl chloride into the *chloride*,

$$CO_2Me{\cdot}C_6H_4{\cdot}COCl,$$

which reacts with cold concentrated aqueous ammonia to form the *amide*-ester, $CO_2Me{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$, m. p. 148·5° (corresponding with I A above); by hydrolysis with methyl-alcoholic sodium hydroxide, the amide-ester yields the *amic-acid*, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$, m. p. 280° (I B). The amic-acid (II B), obtained by treating methyl hydrogen *iso*phthalate with methyl-alcoholic ammonia, has m. p. 280°, is identical with the preceding amic acid, and is converted into the amide-ester, m. p. 148·5° (II A, identical with I A), by shaking the potassium salt obtained from it by methyl-alcoholic potassium methoxide with methyl sulphate. *Ethyl hydrogen* iso*phthalate*, prepared like the corresponding methyl ester, has m. p. 115—117°.

*Methyl 2-nitro*iso*phthalate*, $NO_2{\cdot}C_6H_3(CO_2Me)_2$, m. p. 135°, obtained by

boiling the acid with methyl alcohol and concentrated sulphuric acid, is converted into the following compounds by reactions similar to the preceding. *Methyl hydrogen 2-nitroisophthalate*, $CO_2H\cdot C_6H_3(NO_2)\cdot CO_2Me$, m. p. 197°; *ester-chloride*, m. p. 121°; *ester-amide*, m. p. 190—191°; *amic-acid*, m. p. 252°.

Methyl hydrogen 2-hydroxy*iso*phthalate, by treatment with aqueous methyl-alcoholic ammonia, yields the *amic acid*,

$$CO_2H\cdot C_6H_3(OH)\cdot CO\cdot NH_2,$$

m. p. 245° (decomp.), which is converted into the *amide-ester*, $CO_2Me\cdot C_6H_3(OH)\cdot CO\cdot NH_2$, m. p. 185°, by treatment with potassium methoxide, and subsequently with methyl sulphate, as above. Attempts to prepare the ester-chloride, $CO_2Me\cdot C_6H_3(OH)\cdot COCl$, have not been very successful. Methyl hydrogen 2-hydroxy*iso*phthalate is dehydrated by thionyl chloride, yielding a *substance*, $C_9H_6O_4$, which is probably a multimolecular β-lactone,

$$\left(CO_2Me\cdot C_6H_3{<}{\overset{O}{\underset{CO}{|}}}\right)_x,$$

is converted by acetyl chloride and phosphorus pentachloride into the acetylated anhydride described below, and reacts with phosphorus pentachloride alone to form an impure ester-chloride, from which, however, an ester-amide, m. p. 185°, identical with the above, can be prepared.

Methyl hydrogen 2-hydroxy*iso*phthalate is converted by acetic anhydride and one drop of concentrated sulphuric acid at 40—50° into the *acetoxy*-derivative, $CO_2Me\cdot C_6H_3(OAc)\cdot CO_2H$, m. p. 118—119°, but when heated with acetyl chloride on the water-bath, yields an acetylated *anhydride*, $C_{22}H_{18}O_{11}$, m. p. 144—146°, which does not give a colour reaction with ferric chloride, and is only slowly converted into the original ester-acid by hot water.

When boiled with methyl alcohol and sulphuric acid, 2-hydroxy*iso*phthalic acid yields the *methyl* ester, $OH\cdot C_6H_3(CO_2Me)_2$, m. p. 72°, the potassium salt of which, obtained by interaction with methyl-alcoholic potassium methoxide, reacts with the calculated quantity of methyl sulphate, diluted with twice its weight of benzene, to form a *substance*, $C_{11}H_{12}O_5$, b. p. 170—171°/11 mm., to which the constitution $CO_2Me\cdot C_6H_3{<}{\overset{O}{\underset{C(OMe)_2}{|}}}$ is given. When the potassium salt is heated with methyl sulphate alone, it is converted into a *substance*, $C_{11}H_{12}O_8S$, m. p. 110°, which has acidic properties, develops a wine-red coloration with ferric chloride in aqueous acetone, and retains its sulphur after being boiled with hydrochloric acid; probably it is the trimethyl ester of 2-hydroxy-5-sulpho-*iso*phthalic acid. C. S.

Δ^1-Tetrahydrobenzaldehyde from *cyclo*Hexanone. WALTHER BORSCHE and R. SCHMIDT (*Ber.*, 1910, 3400—3401).—*o-Hydroxyhexahydrobenzylaniline*, $OH\cdot C_6H_{10}\cdot CH_2\cdot NHPh$, obtained by reducing the anil of hydroxymethylene*cyclo*hexanone (Abstr., 1910, i, 881) with sodium and boiling alcohol, crystallises from dilute alcohol in colourless plates, m. p. 98—100°, and on oxidation with chromic anhydride in glacial acetic acid solution yields aniline-black and Δ^1-tetrahydrobenzaldehyde (Wallach, Abstr., 1906, i, 565). The method is not a suitable one for

the preparation of the aldehyde, as the yield is only about 10% of the theoretical (compare Farbwerke vorm. Meister, Lucius & Brüning, Abstr., 1902, i, 102). J. J. S.

Anthranil. XVIII. Methods of Preparation of *o*-Nitrosobenzaldehyde. EUGEN BAMBERGER and ANDOR FODOR (*Ber.*, 1910, **43**, 3321—3335).—For one reason or another *o*-nitrosobenzaldehyde cannot be prepared by the oxidation of *o*-hydroxylaminobenzaldehyde, the electrolytic reduction of *o*-nitrobenzaldehyde, the reduction of *o*-nitrobenzyl chloride by zinc and acetic acid, or by the oxidation of *o*-hydroxylaminobenzaldoxime or of anthranilphenylhydrazine by ferric chloride. It can be prepared by the following methods, none of which, however, are really satisfactory: (1) Hydrochloric acid and sodium nitrite are allowed to react with anthranil under the conditions mentioned by Bamberger and Lublin (Abstr., 1909, i, 509), and the resulting white, crystalline crust on the sides and bottom of the vessel is separated mechanically from the yellow precipitate of *o*-aldehydophenylnitrosohydroxylamine, washed with water at 0°, and purified by distillation with steam. (2) It has been isolated from the products of the hydrolysis of *o*-aldehydophenylnitrosohydroxylamine by dilute sulphuric acid (*loc. cit.*). (3) An alkaline solution of *o*-aldehydophenylnitrosohydroxylamine is treated with not too large a quantity of 3% potassium permanganate at 0°; the ethereal extract of the resulting solution contains *o*-nitrosobenzaldehyde. It is also formed when the oxidation is performed in 2*N*-sulphuric acid at 0°. (4) The oxidation of anthranil in 2*N*-sulphuric acid at 0° by 3% potassium permanganate also yields *o*-nitrosobenzaldehyde; when too much of the oxidising agent is added, *o*-nitrobenzaldehyde is produced; p-*nitrophenylhydrazone*, m. p. 257·5—258·5° (decomp.). The production of *o*-nitrosobenzaldehyde by the oxidation of anthranil furnishes a final argument against Heller's contention, that anthranil and methylanthranil are not similarly constituted homologues, because the former yields *oo'*-azoxybenzoic acid, the latter *o*-nitrosoacetophenone, by oxidation (Abstr., 1908, i, 267; compare also Bamberger and Lublin, *loc. cit.*).

o-Nitrosobenzaldehyde has m. p. 113—113·5° with previous blackening, not 109—110° as stated previously. It can be purified by very rapid distillation with steam, although the loss by decomposition is great. Its solutions have a grass-green colour, which is generally intensified by warming. C. S.

Persulphides of Aldehydes. GÜNTHER BUGGE and IGNAZ BLOCH (*J. pr. Chem.*, 1910, [ii], **82**, 512—519. Compare this vol., i, 46). —To 18 grams of freshly distilled benzaldehyde are gradually added 4·5 c.c. of pure hydrogen disulphide. The liquid becomes warm, turns yellow in colour, and after a time gives a white precipitate of *dibenzylidene disulphide hydroxide*, OH·CHPh·S·S·CHPh·OH; silvery plates or prisms from carbon disulphide; very stable when pure, but decomposes on heating; the molecular weight, determined cryoscopically in bromoform solution, was 257. It is decomposed by alcoholic potassium hydroxide, potassium polysulphide, potassium benzoate, and benzyl alcohol being produced, but no phenylcarbithionic acid. On heating with zinc chloride, it gives a condensation product,

from which phenylcarbithionic acid is readily obtained. The same condensation product may also be obtained in the cold by treatment with hydrogen persulphide.

Dibenzylidene trisulphide dihydroxide, $OH\cdot CHPh\cdot S_3\cdot CHPh\cdot OH$, is similarly obtained from benzaldehyde and hydrogen trisulphide; white prisms from carbon disulphide; it is much less stable than the disulphide hydroxide, showing a great tendency to lose sulphur, but is similar to it in its reactions.

Dianisylidene disulphide dihydroxide, $[OMe\cdot C_6H_4\cdot CH(OH)]_2S_2$, and *dianisylidene trisulphide dihydroxide*, $[OMe\cdot C_6H_4\cdot CH(OH)]_2S_3$, are similar in properties to the dibenzylidene compounds. The trisulphide hydroxide is very unstable, sinters at 25°, m. p. 47—55° with decomposition.

The preparation of *dicinnamylidene disulphide dihydroxide*,

$$[CHPh{:}CH\cdot CH(OH)]_2S_2,$$

is not always successful; it forms white crystals, which sinter at 26° and decompose between 37° and 40°, and unites with bromine, as also does *dicinnamylidene trisulphide hydroxide*, $[CHPh{:}CH\cdot CH(OH)]_2S_3$; this forms white crystals, decomposing at 35°, which at times are very unstable.

The additive compounds of salicylaldehyde with the hydrogen persulphides could not be obtained pure, as they are only stable below −10°. T. S. P.

Hydropinenealdehyde and Hydropinenecarboxylic Acid. JOSEF HOUBEN and HANS DOESCHER (*Ber.*, 1910, **43**, 3435—3442. Compare Abstr., 1908, i, 27).—A somewhat modified method for the preparation of hydropinenealdehyde is described; when carefully sublimed it is obtained as colourless needles, m. p. 131°. The oxime, when boiled with acetic anhydride for three hours, yields the *nitrile* of hydropinenecarboxylic acid, $\begin{array}{l}CH_2{-}CH{-}{-}{-}{-}CH_2\\ \;\;|\qquad\quad >CMe_2\;\;|\\ CH_2\cdot CMe{-}{-}{-}CH\cdot CN\end{array}$, which crystallises from 60% alcohol in slender needles, m. p. 163°. The aldehyde gives Doebner's reaction with β-naphthylamine and pyruvic acid (Abstr., 1894, i, 261, 532), yielding the *β-naphthacinchonic acid*, $C_{10}H_{16}<\begin{array}{l}N{=}{=}{=}{=}C\cdot C_{10}H_7\\ C(CO_2H){:}CH\end{array}$, m. p. 294°.

The hydropinenecarboxylic acid, obtained by oxidising the aldehyde by exposure to the air, crystallises from 60% alcohol, and has m. p. 88—90°, after sintering at 80°. The acid prepared from magnesium pinene hydrochloride has m. p. 72—74° (Houben, Abstr., 1906, i, 21), and from bornyl iodide, 69—71° (Zelinsky, *ibid.*, 1903, i, 185). The *ethyl* ester, $C_{13}H_{22}O_2$, is a pleasant-smelling oil, with b. p. 116—117°/12·5 mm.; it can be obtained pure by the esterification of the acid or in an impure form by the action of ethyl chloroformate on magnesium pinene hydrochloride, and on hydrolysis yields an acid, m. p. 82°, the analytical data of which do not agree with those of a hydropinenecarboxylic acid. The *anhydride*, $(C_{10}H_{17}\cdot CO)_2O$, can be prepared by heating the acid with excess of acetyl chloride, removing the excess, and heating the residue at 200° under atmospheric pressure; it crystallises from alcohol in small needles, m. p. 210°, and when boiled

with 5% potassium hydroxide solution yields an acid, m. p. 78°. The *amide*, $C_{10}H_{17}\cdot CO\cdot NH_2$, is formed together with the ammonium salt of the acid by the action of dry ammonia on a chloroform solution of the anhydride. It crystallises from light petroleum in small prisms, m. p. 138—139°. The *anilide*, $C_{10}H_{17}\cdot CO\cdot NHPh$, crystallises in glistening, felted needles, m. p. 151°.

The acid obtained from the aldehyde appears to be a mixture.

J. J. S.

Action of Sodium Disulphide on 4-Nitro-2-methoxytoluene. JAN J. BLANKSMA (*Rec. trav. chim.*, 1910, **29**, 407—409).—4-Nitro-2-methoxytoluene was prepared by the method of Nölting and Collin (Abstr., 1884, ii, 1006). When it is treated with sodium sulphide and sulphur and distilled, the distillate yields colourless crystals of 2-*methoxy*-p-*toluidine*, m. p. 58°; the *acetyl* derivative crystallises in colourless leaflets, m. p. 130°. The residue after distillation yields 4-*amino*-2-*methoxybenzaldehyde* as colourless crystals, m. p. 136°; the *acetyl* derivative melts at 145°.

4-Hydroxy-2-methoxybenzaldehyde and 2 : 4-dimethoxybenzaldehyde were also prepared from 4-amino-2-methoxybenzaldehyde. N. C.

Some Derivatives of 3-Nitrocumaldehyde. G. PIZZUTI (*Gazzetta*, 1910, **40**, ii, 236—241).—3-*Nitrocumaldehydeoxime*,

$$C_{10}H_{12}O_3N_2,$$

crystallises in colourless needles, m. p. 74—76°, which become reddish-yellow in the light. 3-*Nitrocumaldehydephenylhydrazone*, $C_{16}H_{17}O_2N_3$, forms red scales, m. p. 123° (giving a yellow liquid), and also long, red needles, m. p. 120°. 3-*Nitrocumaldehydesemicarbazone*, $C_{11}H_{14}O_3N_4$, crystallises in rosettes of colourless needles, m. p. 222° (previously softening); when exposed to light, the substance becomes yellow. 3-Nitrocumaldehyde condenses with rhodanic acid, yielding 3-*nitro*-4-iso*propylbenzylidenerhodanic acid*, $C_{13}H_{12}O_3N_2S_2$ (compare Bargellini, Abstr., 1906, i, 536), which forms bright yellow scales, m. p. 180°. The compound dissolves in concentrated sulphuric acid, producing a pale yellow coloration. When 3-nitrocumaldehyde is warmed with 1 molecule of phenylmethylpyrazolone in alcoholic solution, a *compound*, $C_{19}H_{19}O_3N_3$, resulting from the combination of equimolecular quantities of the two substances, is obtained. It forms yellow scales, which begin to decompose at 180°, and at 205—208° are completely fused and decomposed, with production of a red liquid. When two molecules of the pyrazolone are taken in the reaction, a *compound* containing 10·66—10·69% of nitrogen is obtained. It crystallises in pale yellow needles, m. p. 151—153° (becoming red at 140°). When kept at 100°, it loses 4% in weight. The substance remaining contains the same percentage of nitrogen as the compound $C_{19}H_{19}O_3N_3$ mentioned above, but it still has m. p. 153°. R. V. S.

Trimethylene [*cyclo*Propane] Derivatives. LOUIS MICHIELS (*Bull. Soc. chim. Belg.*, 1910, **24**, 396—416).—A number of *cyclo*-propane derivatives have been prepared, and their interaction with various reagents investigated, with a view to comparing the behaviour of the trimethylene residue with isomeric open-chain groups. The results

show that the trimethylene residue exhibits a specific character, and that in particular the hydrogen atom of the ⁚CH group is less easily replaced than in the corresponding *iso*propyl derivatives. The *cyclo*propyl series of alcohols, whether primary or secondary, are readily esterified by haloid acids (compare Bruylants, Abstr., 1909, i, 226).

cyclo*Propyl propyl ketone*, $COPr^{\alpha}\cdot CH<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, D^{20} 0·9077, n_D^{20} 1·43733, b. p. 150°/747 mm., is a colourless, mobile liquid with a mint-like odour. cyclo*Propyl butyl ketone*, D^{20} 0·8782, n_D^{20} 1·43513, b. p. 171—172°/747 mm., resembles its lower homologue in odour and appearance, as does also cyclo*propyl* iso*butyl ketone*, D^{20} 0·8735, n_D^{20} 1·43282, b. p. 161°/757 mm. These three ketones were prepared by Bruylants' method (*loc. cit.*), using the magnesium alkyl bromide appropriate to each case.

Attempts to prepare *di*cyclo*propyl ketone* by the catalytic action of heated alumina or thoria on *cyclo*propanecarboxylic acid or its ethyl ester were unsuccessful, although in one experiment a *product*, boiling at 160—170°, and yielding a *semicarbazone*, m. p. 85—86°, was obtained.

cyclo*Propyl chloromethyl ketone*, $C_3H_5\cdot CO\cdot CH_2Cl$, D^{20} 1·2036, n_D^{20} 1·46235, b. p. 180°/762 mm., or 103°/40—45 mm., obtained by the action of sulphuryl chloride on *cyclo*propyl methyl ketone, is a colourless, mobile liquid, the vapour of which is irritant to the mucous membrane. It reacts with potassium cyanide, and with sodium ethoxide yields a substance which reduces Fehling's solution.

The ketones described above on reduction by sodium in alcohol furnish the corresponding carbinols, and the following were thus prepared: cyclo*Propylpropylcarbinol*, $OH\cdot CHPr^{\alpha}\cdot CH<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, D^{20} 0·8693, n_D^{20} 1·43663, b. p. 154—155°/750 mm., is a viscous, colourless liquid having a camphoraceous odour. The *acetate*, D^{20} 0·9013, b. p. 174—175°/764 mm., is colourless, mobile, and of agreeable piperaceous odour. cyclo*Propylbutylcarbinol*, D^{20} 0·8721, n_D^{20} 1·43984, b. p. 175°/751 mm., resembles its lower homologue; on saturation with hydrogen bromide it furnishes two monobromo-compounds, the one probably cyclo*propylbutylcarbinyl bromide*, b. p. 150°/40 mm., and the *other*, b. p. 120°/40 mm., probably an ethylenic compound derived from the dibromooctane, D^{20} 1·3145, n_D^{20} 1·48302, obtained when a mixture of the two monobromo-compounds is further treated with hydrogen bromide, the trimethylene ring being thereby opened (compare Dalle, Abstr., 1902, i, 525; Perkin, Abstr., 1902, i, 597; and Demjanoff and Fortunatoff, Abstr., 1907, i, 1033). cyclo*Propyl*iso*butylcarbinol*, D^{20} 0·8648, n_D^{20} 1·43553, b. p. 167°/751 mm., is viscous and possesses a camphoraceous odour. cyclo*Propylethylpropylcarbinol*, $OH\cdot CEtPr^{\alpha}\cdot CH<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, D^{20} 0·8843, n_D^{20} 1·45147, b. p. 178—179°/735 mm., obtained by the action of magnesium ethyl bromide on *cyclo*propyl propyl ketone, is a strong smelling liquid. It yields a *bromide*, b. p. 208°/739 mm. (decomp.), which on treatment with potassium hydroxide in alcohol at 150° furnishes a mixture of

hydrocarbons, D^{20} 0·7894, n_D^{20} 1·43737, b. p. 147—149°/757 mm. (compare Bruylants, *loc. cit.*).

*cyclo*Propylcarbinol is readily esterified by hydrogen bromide in the cold, and from the resulting bromide may be obtained, by treatment with sodium iodide in methyl alcohol, the iodide, which with potassium hydroxide in alcohol gives (1) a small yield of a *hydrocarbon*, possibly $CH{:}CH{<}\begin{matrix}CH_2\\|\\CH_2\end{matrix}$ or $\begin{matrix}CH_2{\cdot}CH\\|\quad\;\;||\\CH_2{\cdot}CH\end{matrix}$ (compare Demjanoff, Abstr., 1908, i, 85), b. p. −3° to 1°, which combines with bromine to form a tetrabromide, $CH_2Br{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2Br$ (?), m. p. 112—114°, and (2) cyclo*propylcarbinyl ethyl ether*, $OEt{\cdot}CH_2{\cdot}CH{<}\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, b. p. 98—101°, a liquid of ethereal odour. With dry potassium hydroxide, but little action occurs, and the ether appears to be the chief product. *cyclo*Propylcarbinyl iodide differs markedly from the isomeric *iso*butyl iodide in its behaviour with potassium hydroxide in alcohol, and similarly, whilst *iso*butyric chloride is readily chlorinated, the chloride of *cyclo*propylcarboxylic acid is recovered practically unchanged after treatment with chlorine. T. A. H.

Action of Hydrazine Hydrate on 1-Methyl*cyclo*hexan-3-one. A. Merkin (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 1204—1211).—When 1-methyl*cyclo*hexan-3-one is treated with hydrazine hydrate, it yields (1) the ketazine, $C_7H_{12}{:}N{\cdot}N{:}C_7H_{12}$, b. p. 229°/140 mm., 210°/71 mm., α −51·59° to −45·84°; (2) 1-*methyl*cyclo*hexan*-3-*onehydrazone*, $CH_2{<}\begin{matrix}CHMe{\cdot}CH_2\\CH_2{-\!-}CH_2\end{matrix}{>}C{:}N{\cdot}NH_2$, b. p. 154°/71 mm., D_0^{17} 0·9603, n_D^{17} 1·5043, $[\alpha]_D$ −35·94°. It is a colourless liquid, which decomposes and turns yellow in air, forms the above ketazine on distillation, and combines with water, forming a crystalline *hydrate*. With benzaldehyde it forms benzaldazine, m. p. 93°, and methyl*cyclo*hexanone, and when reduced with sodium and alcohol, it yields aminomethyl*cyclo*hexane and *methyl*cyclo*hexylmethyl*cyclo*hexylidenehydrazine*,

$$C_7H_{12}{:}N{\cdot}NH{\cdot}C_7H_{13},$$

which with hydrochloric acid yields methyl*cyclo*hexylhydrazine hydrochloride, $C_7H_{13}{\cdot}NH{\cdot}NH_2,HCl$; the free hydrazine has b. p. 208—209°.

The thiosemicarbazide, $NHPh{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}C_7H_{13}$, m. p. 135°, crystallises from methyl alcohol in needles and in rhombic plates, $[\alpha]_D$ −15·94°. By treating methyl*cyclo*hexylhydrazine with pyruvic acid in hydrochloric acid solution, prismatic crystals of the *hydrazone*,

$$C_7H_{13}{\cdot}NH{\cdot}N{:}CMe{\cdot}CO_2H,$$

m. p. 96—98°, $[\alpha]_D'$ −16·62° are produced, together with a *substance*, m. p. 236—237°, $[\alpha]_D$ −11·05°, which is also obtained by treating the hydrazine with hydrochloric acid, and when heated with fuming hydrochloric acid in a sealed tube at 180° is partly converted into a gelatinous mass soluble in alkalis. The methyl*cyclo*hexylhydrazine re-obtained from the methyl*cyclo*hexylhydrazone of pyruvic acid yields a *thiosemicarbazide*, m. p. 135—136°, $[\alpha]_D$ −23·68°, showing that the original hydrazine consists of a mixture of stereoisomeric hydrazines.

The ketazine, $C_7H_{12}{:}N_2{:}C_7H_{12}$, when treated with hydrazine hydrate

and solid potassium hydroxide on a water-bath, is partly converted into 1-*methylcyclohexan-3-onehydrazone*. Z. K.

Compounds of Aluminium Chloride and Bromide with Acetophenone and Benzophenone. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1298—1307).—Aluminium bromide reacts more readily with benzophenone than does the chloride. It forms a crystalline, molecular compound, $AlBr_3,COPh_2$, m. p. 142°, which is instantly decomposed by water, with formation of benzophenone. The solubility curve of the two substances is very similar to those obtained for aluminium bromide with the nitro-derivatives of aromatic hydrocarbons and their derivatives (Abstr., 1909, i, 900; 1910, i, 234). It has two eutectic points, at 38° and composition $AlBr_3,4{\cdot}51COPh_2$, and at the same temperature but composition $AlBr_3,0{\cdot}49COPh_2$. Aluminium chloride also forms a molecular compound, $AlCl_3,COPh_2$, m. p. 130° (Perrier gives 119°). The solubility curve has two eutectic points, at 39·5° and composition $AlCl_3,4{\cdot}92COPh_2$, and at 60° at the composition $AlCl_3,0{\cdot}57COPh_2$. When working with these substances it is best to use no third substance, such as sulphuric acid, as solvent. Aluminium halides with acetophenone also yield molecular compounds, but the system is difficult to investigate, since the salts crystallise very slowly, and readily yield resinous products.

Curves and tables are given. Z. K.

Organic Syntheses by means of Sunlight. V. Behaviour of Acids and Ethers [including Esters] with Benzophenone. EMANUELE PATERNÒ and G. CHIEFFI (*Gazzetta*, 1910, **40**, ii, 321—331. Compare Abstr., 1909, i, 240; 1910, i, 41).—Acetic acid and benzophenone do not react when exposed to sunlight. Propionic acid and benzophenone yield a small quantity of a yellow, resinous acid *substance*. Benzophenone and butyric acid give benzopinacone and a yellow *resin*, m. p. 74—75°, which has the properties of an acid, and contains both benzophenone and butyric acid groups. Between benzophenone and benzoic acid no reaction occurs. Phenylacetic acid and benzophenone yield benzopinacone and *β-hydroxy-αββ-triphenylpropionic acid*, $OH{\cdot}CPh_2{\cdot}CHPh{\cdot}CO_2H$, which forms small, flat needles, m. p. 205—208°. The *silver* salt was prepared. Phenylpropionic acid and benzophenone give benzopinacone, an *acid*, m. p. 271—273°, and a substance, m. p. 161—163°. These two products, however, contain traces of benzopinacone. The acid has the formula $C_{18}H_{18}O_4$, and is either diphenyladipic acid,

$$CO_2H{\cdot}CH_2{\cdot}CHPh{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H,$$

or dibenzylsuccinic acid. It resists boiling with nitric acid, and does not decolorise permanganate. The substance of m. p. 161—163° has the formula $C_{22}H_{18}O_2$, and is probably the *lactone*,

$$\begin{array}{l}CH_2\text{——}CO\\ |\\ CHPh{\cdot}CPh_2\end{array}\!\!>\!O.$$

Benzophenone reacts with ethyl ether, producing benzopinacone and a *resin*, $C_{17}H_{18}O_2$, which in the authors' opinion probably has the structure $CPh_2{<}\begin{smallmatrix}O\\CH_2\end{smallmatrix}{>}CH{\cdot}OEt$, although owing to the difficulty of

purifying the substance some of the analytical results do not agree very well with that formula. Benzophenone and *iso*amyl ether yield benzopinacone, a heavy, viscous *oil*, the analysis of which agrees with the formula $C_{23}H_{32}O_2$ required by a product analogous to that from ethyl ether. Acetal and benzophenone give benzopinacone and a heavy *oil*. Glycerol dimethyl and diethyl ethers behave similarly. Amyl formate and benzophenone yield benzopinacone and a heavy, viscous oil, which appears to be a *lactone* analogous to that obtained from phenylpropionic acid. The formation of benzopinacone was also observed when benzophenone was kept in sunlight with ethyl acetate, ethyl ethylmalonate, ethyl tartrate, the methyl ethers of *m*-cresol, *p*-cresol and resorcinol, and with ethyl phenylpropionate. In most cases the formation of resinous substances was also noted. Benzophenone and benzyl acetate yield in addition to benzopinacone, a *substance*, m. p. 218—219° (compare following abstract). R. V. S.

Organic Syntheses by means of Sunlight. VI. The Product of the Reaction between Benzophenone and Benzyl Acetate. Emanuele Paternò and G. Forlì-forti (*Gazzetta*, 1910, **40**, ii, 332—341. Compare preceding abstract).—The substance forms small, hard, colourless crystals, and has the formula, $C_{22}H_{20}O_3$, of an additive product of equimolecular quantities of benzophenone and benzyl acetate. The authors ascribe to it the structure of the *acetyl* derivative of *triphenylethylene glycol*, $OH\cdot CPh_2\cdot CHPh\cdot OAc$, and advance the following reasons in support of this formula: (1) when the substance is heated with alcoholic potassium hydroxide, benzhydrol, benzoic acid, and acetic acid are formed; (2) when heated with alcohol in a sealed tube at 200° for eight hours, the compound yields ethyl acetate and a substance, $C_{20}H_{16}O$, m. p. 134—135°, apparently identical with triphenylvinyl alcohol (Biltz, Abstr., 1899, i, 439), which is a product of dehydration of triphenylethylene glycol; (3) by the action of acetyl chloride on the substance, triphenylvinyl alcohol is obtained, whilst acetyl chloride in presence of acetic acid leads to the formation of a *substance* crystallising in needles, m. p. 103—105°, which has the composition of an acetyl derivative of that alcohol.
R. V. S.

Some Properties of Piperonyloin. Henry A. Torrey and J. B. Sumner (*J. Amer. Chem. Soc.*, 1910, **32**, 11, 1492—1494).—The piperonyloin was prepared by Perkin's method (Trans., 1891, **59**, 150), some modifications being introduced. A comparison was made of the behaviour of piperonyloin and of benzoin under similar conditions, and it was found that piperonyloin is much less reactive than benzoin; thus it is not affected by reducing agents or acetyl chloride, and it does not form an oxime. The only substances found with which it reacts easily are carbamide and ammonium thiocyanate. *Piperonyloincarbamide*, $C_{17}H_{12}O_5N_2$, forms pale pink crystals, decomposing at 265°. The *thiocarbamide* crystallises in long, felted, nearly white needles, decomposing at 260°, and probably has the formula $C_{17}H_{12}O_4N_2S$. N. C.

Allyloxanthranol and Some of its Derivatives. H. Kondo (*Ber.*, 1910, **43**, 3182—3187).—The investigation was undertaken with the object of preparing benzanthrone (Bally, Abstr., 1905, i, 237).

9-*Allyloxanthranol*, $CO<_{C_6H_4}^{C_6H_4}>C(OH)\cdot C_3H_5$, is prepared in a similar manner to amyloxanthranol (compare Liebermann, Abstr., 1882, 855; Liebermann and Roka, Abstr., 1908, i, 427) by the action of allyl bromide on anthraquinone. It crystallises in large, colourless, measurable crystals, m. p. 108°. On reduction with sodium amalgam, 9-propyloxanthranol, m. p. 164° (Hallgarten, Abstr., 1889, 894), is formed.

With hydrogen bromide, 9-*β-bromopropyloxanthranyl bromide*, $CO<_{C_6H_4}^{C_6H_4}>CBr\cdot CH_2\cdot CHBrMe$, is obtained in colourless, prismatic crystals, m. p. 129°. With bromine in carbon disulphide solution, 9-*αβ-dibromopropyloxanthranol*, $CO<_{C_6H_4}^{C_6H_4}>C(OH)\cdot C_3H_5Br_2$, is obtained; it crystallises in colourless, slender prisms, m. p. 147°.

The elimination of hydrogen bromide from the dibromide is incomplete in presence of pyridine and quinoline. With alcoholic potassium hydroxide, heat is required to render it complete, and decomposition products are readily formed. On the addition of acid, a compound, $C_{17}H_{12}O_2$, possibly allylenyloxanthranol, is obtained of a faint yellow hue, m. p. 111°. It gives a green coloration with concentrated sulphuric acid. With bromine in carbon disulphide, a small quantity of a blood-red, crystalline precipitate is formed, which is very easily decomposed, becoming yellow. With dilute alkali hydroxides, a yellow potassium salt is obtained, which fluoresces like eosin in alcoholic solution.

From the carbon disulphide mother liquors a yellow compound, 9-*dibromomethyleneanthrone*, $CO<_{C_6H_4}^{C_6H_4}>C{:}CBr_2$, m. p. 167°, is obtained, which is quantitatively converted into anthraquinone by moisture.

E. F. A.

Some Derivatives of 2-Acetyl-α-naphthol. Henry A. Torrey and E. J. Cardarelli (*J. Amer. Chem. Soc.*, 1910, **32**, ii, 1477—1488). —2-Acetyl-α-naphthol was prepared by Friedländer's method (Abstr., 1895, i, 668), and various derivatives obtained and examined. During experiments on the action of benzaldehyde on 2-acetyl-α-naphthol, a second form of 2-acetyl-α-naphthol was obtained in brown plates, m. p. 98°, instead of the original yellowish-green needles, m. p. 103°. It is thought that the brown form has a quinonoid structure, and that the yellow form is the phenol. Several methods were tried, unsuccessfully, to obtain a quinoline from 2-acetyl-α-naphthol.

4-Amino-2:(?)-diacetyl-α-naphthol forms yellowish-white needles, arranged like chestnut burs, and melting at 212°. Friedländer gives m. p. 107° for this compound, but the authors could not obtain this melting point.

4-Amino-2-acetyl-α-naphthol reacts quantitatively with aldehydes;

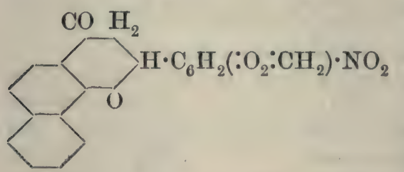
4-*benzylideneamino-2-acetyl-α-naphthol* forms plates between the colours of brass and bronze, m. p. 159°; the corresponding *piperonylidene* derivative crystallises in brown plates, m. p. 178°, and the *cinnamylidene* derivative in brownish-yellow needles, m. p. 144°.

4-*Nitro-2-cinnamoyl-α-naphthol*, $OH\cdot C_{10}H_5(NO_2)\cdot CO\cdot CH\colon CHPh$, crystallises in two forms, a yellow one and a red one; the melting point varies from 202° to 208°. 2-m-*Nitrocinnamoyl-α-naphthol* forms red, microscopic needles, m. p. 210°; it absorbs bromine easily, forming a vermilion-coloured substance. By the action of sodium hydroxide on a mixture of 2-acetyl-α-naphthol and 6-nitropiperonal, the ketol, 2-(*β-hydroxy-β-6′-nitropiperonylpropionyl*)-*α-naphthol*,

$$CH_2O_2\colon C_6H_2(NO_2)\cdot CH(OH)\cdot CH_2\cdot CO\cdot C_{10}H_6\cdot OH,$$

is obtained. It forms lemon-yellow needles, m. p. 201—202°.

The *monoacetate* of the ketol crystallises in cream needles, m. p. 188—190°; it forms a *tribromo*-derivative. The *diacetate* of the ketol forms golden, rectangular crystals, m. p. 197—198°. By the action of bromine on the ketol, two *substances* are obtained, one red, m. p. 252°, and one yellow, m. p. 220°.



2-(6-*Nitropiperonyl*)-*naphthaflavanone* (annexed formula) crystallises in red needles with an orange tinge, m. p. 226°; bromine acts on it to give the *substance*, $C_{20}H_{12}O_6NBr$, which forms an orange powder decomposing at 250—255°. N. C.

Some Derivatives of Hydroxyquinol. I. and II. GUIDO BARGELLINI and GHERSCH AVRUTIN (*Gazzetta*, 1910, 40, ii, 342—347, 347—353. Compare Reigrodski and Tambor, Abstr., 1910, i, 578).—I. In some of their results the authors have been anticipated by the publication cited above. 2 : 4 : 5-Trimethoxyacetophenone has b. p. 285—290°/33 mm. When oxidised with permanganate, it yields asaronic acid. Its *oxime* forms colourless crystals, m. p. 126—127°. The *semicarbazone* crystallises in small laminæ, m. p. 186—188°. 2 : 4 : 5-Trimethoxychalkone has m. p. 117—118° (Reigrodski and Tambor gave 113—114°). 4 : 2′ : 4′ : 5′-*Tetramethoxychalkone* (from trimethoxyacetophenone and anisaldehyde) crystallises in small, yellow needles, m. p. 123—124°, and dissolves in concentrated sulphuric acid, producing an intense red coloration. 3 : 4 : 2′ : 4′ : 5′-*Pentamethoxychalkone* (from veratraldehyde) forms yellow scales, m. p. 155°, and gives a red coloration when dissolved in concentrated sulphuric acid. 3 : 4-*Methylenedioxy-2′ : 4′ : 5′-trimethoxychalkone* (from piperonaldehyde) crystallises in yellow laminæ, m. p. 182—183°. It gives a reddish-violet coloration with concentrated sulphuric acid.

II. When triacetylhydroxyquinol is heated with acetic acid and zinc chloride, or with chloroacetic acid and zinc chloride, or with zinc chloride alone, a mixture of two substances is obtained, namely, a red *compound*, crystallising in needles, m. p. 200—202° (decomp.), and a colourless *substance*, crystallising in silvery scales, m. p. 165—166°. Both have the composition $(C_2H_2O)_n$, which agrees with that of

trihydroxyacetophenone and its three acetyl derivatives. Both substances yield trimethoxyacetophenone when treated with methyl sulphate. R. V. S.

Turmeric Oil. II. Oxidation Products of Curcumone. HANS RUPE and A. STEINBACH (*Ber.*, 1910, **43**, 3465—3471. Compare Rupe, Lucksch, and Steinbach, Abstr., 1909, i, 598).—Potassium permanganate is the only oxidising agent which, by its attack on curcumone, gives some insight into the constitution of the ketone. When curcumone is treated with 4% potassium permanganate at the ordinary temperature, *p*-tolyl methyl ketone, terephthalic acid, and *p*-acetylbenzoic acid are produced. When curcumone is shaken for eight hours with aqueous sodium hypobromite at 0° in a bottle protected from light, a considerable quantity of the ketone is recovered unchanged, together with bromoform and an *acid*, $C_{12}H_{16}O_2$, m. p. 33—34°, b. p. 168—170°/12 mm., $[\alpha]_D^{20}$ 31·15° in alcohol, which is purified best through the *calcium* salt, $Ca(C_{12}H_{15}O_2)_2,3H_2O$; it receives the name *curcumic acid*, and is apparently identical with Jackson and Menke's turmeric acid. A small quantity of another *acid*,

$C_{12}H_{16}O_3(?)$,

m. p. 150—151°, has also been isolated, which is oxidised to terephthalic acid by potassium permanganate. The oxidation of curcumic acid by 4% potassium permanganate in the presence of sodium carbonate at 0° yields *p*-tolyl methyl ketone, terephthalic acid, and a dibasic *acid*, $C_{12}H_{14}O_4$, m. p. 226—228°, which may be identical with Jackson and Menke's *apo*turmeric acid, m. p. 221°.

The preceding results indicate that curcumone, $C_{13}H_{18}O$, is a derivative of benzene containing two para-substituents, one of which is methyl, and the second, one or other of the groups

$\cdot CHMe\cdot CH_2\cdot CH_2\cdot COMe$,

$\cdot CHMe\cdot CHMe\cdot COMe$, or $\cdot CMeEt\cdot COMe$. Curcumic acid contains a carboxyl group in the place of the group $\cdot COMe$. C. S.

Dianilino-*p*-benzoquinoneanil. WILLIAM KÜSTER (*Ber.*, 1910, **43**, 2962—2964).—The compound obtained by Küster and Fuchs (Abstr., 1907, i, 572) by the action of aniline on hæmin is now shown to be dianilino-*p*-benzoquinoneanil and to be free from iron. Apparently hæmin acts as a ferric salt, and brings about to some extent the oxidation of aniline at the ordinary temperature. E. F. A.

Nitranilic Acid [3 : 6-Dinitro-2 : 5-dihydroxy-*p*-benzoquinone]. RUDOLF NIETZKI (*Ber.*, 1910, **43**, 3457—3459).—Potassium nitroanilate is obtained in 75—80% yield by adding the paste, obtained by stirring quinol with acetic anhydride and a few drops of concentrated sulphuric acid, to cold nitric acid, D 1·48, adding subsequently concentrated sulphuric acid, and pouring the mixture, after being kept for twelve hours at 0°, on to ice; the solid product is treated with ice and potassium hydroxide (compare Henle, *Annalen*, 1906, **350**, 334). C. S.

Action of Hydroxylamine on Some Ortho-substituted Derivatives of Anthraquinone. MARTIN FREUND and FRITZ ACHENBACH (*Ber.*, 1910, **43**, 3251—3260).—*o*-Chlorinated anthra-

quinones react with hydroxylamine more readily than anthraquinone itself, and the oximes formed lose hydrogen chloride when boiled with alkali, yielding cyclic compounds resembling those prepared by Meyer and Cathcart from *o*-halogenated benzophenones (Abstr., 1892, 992; 1893, i, 94).

1-Chloroanthraquinone reacts with hydroxylamine hydrochloride and alcohol at 180°, yielding a mixture of two oximes, but when these are boiled with dilute sodium hydroxide solution, the one, presumably the *syn*-compound, is transformed into anthrone*iso*oxazole,

$$\begin{array}{l} C_6H_4\cdot C{=}N \\ | \qquad\quad | \\ CO - C_6H_3 \end{array}\!\!>\!O,$$

whereas the other, the *anti*oxime, is not decomposed.

1 : 5-Dichloroanthraquinone and hydroxylamine hydrochloride at 185° yields a mixture of oximes, and when these are boiled with alkalis an insoluble product consisting of a mixture of 5-chloro-10-anthrone-1 : 9-*iso*oxazole, $\begin{array}{l} C_6H_3Cl\cdot C{=}N \\ | \qquad\qquad | \\ CO - - C_6H_3 \end{array}\!\!>\!O$, and anthradi*iso*oxazole,

$$\begin{array}{l} O{:}C_6H_3\cdot C{=}N \\ | \;\; | \qquad\quad | \\ N{:}C - - C_6H_3 \end{array}\!\!>\!O,$$

is formed together with two oximes which remain dissolved in the alkali; these are the *anti*-forms of the mono- and di-oximes of 1 : 5-dichloroanthaquinone.

*Anthrone*iso*oxazole*, $C_{14}H_7O_2N$, crystallises from hot chlorobenzene in slender, nearly colourless needles, m. p. 298·5°. 1-*Chloroanthraquinone*-anti-*monoxime*, $C_{14}H_8O_2NCl$, crystallises from a mixture of methyl alcohol and water in golden-yellow plates, m. p. 219—222° (decomp.). 1 : 5-*Dichloroanthraquinone*-anti-*monoxine*, $C_{14}H_7O_2NCl_2$, crystallises from hot glacial acetic acid in yellow needles, m. p. 252° after sintering at 235°.

1:5-*Dichloroanthraquinone*-anti-anti-*dioxime*, $C_{14}H_8O_2N_2Cl_2$, is, unlike the monoxime, insoluble in hot chlorobenzene, and forms a grey powder, m. p. 245° (decomp.).

1-*Chloroanthrone*iso*oxazole*, $C_{14}H_6O_2NCl$, crystallises from glacial acetic acid, and has m. p. 229° after sintering at 225°. *Anthradi*iso*oxazole*, $C_{14}H_6O_2N_2$, is sparingly soluble in hot chlorobenzene, and has m. p. 304°.

1-*Methoxyanthraquinonemonoxime*, $C_{15}H_{11}O_3N$, crystallises from alcohol in dark brown needles, m. p. 198°. The corresponding 1-*phenoxy*-derivative, $C_{20}H_{13}O_3N$, crystallises from 75% acetic acid in brown needles, m. p. 175° after sintering at 155°.

The *monoxime* of anthrarufin dimethyl ether, $C_{16}H_{13}O_4N$, has m. p. 196° after sintering at 185°. J. J. S.

Action of Bornyl Chloride on Aromatic Amines. FRITZ ULLMANN and ALFRED SCHMID (*Ber.*, 1910, 43, 3202—3209).—Bornyl chloride reacts with primary aromatic amines, yielding a mixture of camphene and bornylarylamine.

Bornylaniline, $C_{10}H_{17}\cdot NHPh$, obtained by boiling a mixture of bornyl chloride and aniline for three hours, is a colourless, strongly refractive, viscid liquid, b. p. 140°/2 mm., and forms a *hydrochloride*,

m. p. 198°, and an *acetyl* derivative, m. p. 123°. On nitration, the latter yields *acetobornyl*-p-*nitroanilide*, $C_{10}H_{17}\cdot NAc\cdot C_6H_4\cdot NO_2$, white, glistening leaflets, m. p. 185°.

Acetylbornyl-p-*phenylenediamine*, $C_{10}H_{17}\cdot NAc\cdot C_6H_4\cdot NH_2$, obtained by reducing the nitro-compound with stannous chloride and hydrochloric acid, crystallises in colourless needles, m. p. 148°.

When bornyl chloride is boiled with aniline and the product distilled under ordinary pressure, a 96% yield of camphene is obtained.

Bornyl-o-*toluidine*, $C_{10}H_{17}\cdot NH\cdot C_6H_4\cdot Me$, prepared from bornyl chloride and *o*-toluidine, crystallises in needles, m. p. 55°, b. p. 160°/4 mm.; the *hydrochloride* has m. p. 180°.

Bornyl-p-*toluidine* has b. p. 162°/3 mm., crystallises in needles, m. p. 33°, and yields a crystalline *hydrochloride*, m. p. 214° (decomp.).

Bornyl-m-4-*xylidine*, b. p. 176°/7 mm., crystallises from methyl alcohol in large needles, m. p. 79°.

The action of bornyl chloride on *m*-tolylenediamine leads to the formation of camphene and *diamino-ditolylamine*, $C_{14}H_{17}N_3$, glistening, colourless leaflets, m. p. 154—155°.

The same product is obtained by heating *m*-tolylenediamine with its hydrochloride at 200°. The *diacetyl* derivative, has m. p. 247°.

F. B.

Catalytic Reduction. III. ALADAR SKITA and H. RITTER (*Ber.*, 1910, 43, 3393—3399. Compare Abstr., 1908, i, 855; 1909, i, 479).—*d*-Pulegone is reduced by hydrogen under two atmospheres pressure, in presence of colloidal platinum, to *d*-menthone, whilst the product obtained with other reducing agents is *l*-menthone (Beckmann, Abstr., 1889, 721). Phorone yields di*iso*butylcarbinol, whilst mesityl oxide is only reduced to methyl *iso*butyl ketone. This difference may be explained by the different positions of the carbonyl group.

Using a lower pressure of hydrogen (one and a-half atmospheres), phorone may be reduced only to valerone, whilst under as high a pressure as five atmospheres it may be reduced to methyl*iso*butylcarbinol. *iso*Phoroneoxime yields, under four atmospheres, 5-amino-1:1:3-trimethyl*cyclo*hexane.

Phenylacetaldehyde is converted into phenylethyl alcohol, and quinone into quinol. C. H. D.

Action of Hydrazine Hydrate on Thujone. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 1198—1204).—By the action of an excess of hydrazine hydrate on thujone in alcoholic solution, the latter is converted quantitatively into *thujonehydrazone*,

$CH_2<\begin{matrix}CH\cdot CHMe\\ |\\ CPr—CH_2\end{matrix}>C:N\cdot NH_2$, a colourless liquid with a faint odour,

b. p. 149°/35 mm., D_0^{22} 0·9504, n_D^{22} 1·4952, $[\alpha]_D$ +123·75°, which readily reduces ammoniacal silver oxide, and dissolves in hydrochloric acid with formation of thujone, b. p. 202—203·5°/739 mm., α +33·36°; the original thujone had α +65·0°. When reduced with sodium in alcoholic solution, the hydrazone yields *thujylhydrazine*, $C_{10}H_{17}\cdot NH\cdot NH_2$, b. p.

142—144°/38 mm., 242—244°/741 mm., D_0^{20} 0·9302, $[\alpha]_D + 76·67°$, n_D^{20} 1·4800, which is oxidised on exposure to air and reduces ammoniacal silver oxide. Thujone, b. p. 202—204°/739 mm., α +26·28°, and impure thujylamine, b. p. 196—199°, α +50·30°, are formed as by-products. When mixed with phenylthiocarbimide, the hydrazone forms the *phenylthiosemicarbazide*, $NHPh\cdot CS\cdot NH\cdot NH\cdot C_{10}H_{17}$, which forms prismatic needles, m. p. 134·5—135°, $[\alpha]_D$ +51·89° in chloroform solution, whilst with potassium ferricyanide in potassium hydroxide solution the hydrazine yields thujene, b. p. 157·5—158°/741 mm., D_0^{20} 0·8164, n_D^{20} 1·4398, $[\alpha]_D + 53·41°$. Thujene has a faint odour, and reacts very slowly with alkaline potassium permanganate. In chloroform solution it absorbs bromine, forming an unstable *bromide*; it also combines with hydrogen bromide, forming a heavy *bromide*, which when boiled with potassium hydroxide yields an unsaturated *hydrocarbon*, $C_{10}H_{18}$, b. p. 162—165°, D_{20}^{20} 0·8139, n_D^{20} 1·4512, α +3·32°.

Z. K.

Semicarbazide and Cyclic Nitrosochlorides. HANS RUPE and H. ALTENBURG (*Ber.*, 1910, 43, 3471—3474).—The ease with which the semicarbazide group replaces the oximino-group in aliphatic oximino-ketones (Rupe and Kessler, Abstr., 1910, 93) has induced the authors to examine the behaviour of some cyclic nitrosochlorides. An alcoholic solution of *d*-β-bislimonene nitrosochloride is boiled for one hour with a concentrated aqueous solution of semicarbazide hydrochloride. When the product is distilled directly with steam, carvone is obtained, but when the product is first neutralised by sodium hydrogen carbonate and is then distilled with steam, the oxime and the semicarbazone of carvone are obtained. Bisterpineol nitrosochloride, under similar conditions, yields terpineol by direct distillation with steam, the residue containing 8-hydroxydihydrocarvonesemicarbazone. The latter, together with hydrazodicarbonamide, is obtained when potassium acetate is added to the aqueous-alcoholic solution before boiling.

l-Carvoxime is produced when the product of the reaction between magnesium and *d*-limonene nitrosochloride in dry ether is decomposed by cold water and dilute sulphuric acid.

C. S.

Hydrogenation of Isomeric Thujenes and of Sabinene. Thujane. LEO A. TSCHUGAEFF and W. FOMIN (*Compt. rend.*, 1910, 151, 1058—1062. Compare Abstr., 1905, i, 71).—Zelinsky (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 768) has shown that reduction of *l*-α-thujene by Sabatier and Senderens' method leads to rupture of the trimethylene ring and production of a hydrocarbon, $C_{10}H_{20}$. When the reduction, however, is effected at the ordinary temperature by hydrogen and platinum-black, *thujane*, $C_{10}H_{18}$, is obtained; this has b. p. 157°/758 mm., D_4^{16} 0·8161, n_D^{20} 1·43759, $[\alpha]_D$ +62·03°. When prepared from *d*-β-thujene, the product has b. p. 157°/759 mm., D_4^{16} 0·8191, n_D^{16} 1·44102, $[\alpha]_D$ +34·72°, whilst under the same conditions sabinene gives a hydrocarbon, b. p. 157—158°/760 mm., D_4^{17} 0·8190, n_D^{17} 1·44393, $[\alpha]_D$ +18·56°. The hydrocarbons are probably identical, except in their

optical rotations, and their stability towards oxidising agents suggests that they have the constitution $CH_2\left\langle\begin{array}{l}CH{-}CHMe\\ CPr^{\beta}{-}CH_2\end{array}\right\rangle CH_2$.

W. O. W.

Constituents of Ethereal Oils. Regeneration of Caryophyllene. FRIEDRICH W. SEMMLER and ERWIN W. MAYER (*Ber.*, 1910, 43, 3451—3455. Compare Schreiner and Kremers, Abstr., 1902, i, 108; Schimmel & Co., *Bericht*, October, 1910, 173).—By the elimination of hydrogen chloride from caryophyllene dihydrochloride by means of a saturated methyl-alcoholic solution of potassium hydroxide or a concentrated solution of sodium methoxide, a hydrocarbon is obtained with the following properties: b. p. 121—122·5°/12 mm., D_4^{20} 0·8996, α_D +19°, n_D^{20} 1·4990. This hydrocarbon yields the same dihydrochloride, m. p. 69—70°, as is obtained from the original caryophyllene. Both dihydrochlorides are dextrorotatory, although the natural hydrocarbon is lævo- and the regenerated hydrocarbon dextro-rotatory. The conclusion is drawn that the natural hydrocarbon contains the same caryophyllene as the regenerated, but contains, in addition, a lævorotatory compound (compare Deussen and Lewinsohn, Abstr., 1908, i, 353; 1909, i, 171).

The products obtained by eliminating the hydrogen chloride by means of dilute alkalis or of sodium acetate and acetic acid are not homogeneous. When, however, the dihydrochloride is boiled for three-quarters of an hour with quinoline, an isomeric caryophyllene with the following properties is obtained: b. p. 122—123°/13 mm., D_4^{20} 0·927, n_D^{20} 1·50246, and α_D^{20} −57° in a 1-dcm. tube.

This hydrocarbon is regarded as the pure tricyclic caryophyllene.

The following formulæ are suggested:

$$\begin{array}{rcl}CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH & {-}CH{-} & CMe_2\\ | & CH_2 & |\\ CH_2{:}C{-}{-}CH & {-} & CH_2\end{array}\quad\text{and}\quad\begin{array}{lcl}CH{\cdot}CH_2{\cdot}CH & {-}CH{-} & CMe_2\\ |\qquad\quad | & CH_2 & |\\ CMe{\cdot}CH_2{\cdot}CMe & {\cdot}CMe{\cdot} & CH_2\end{array}$$

Recovered caryophyllene. Tricyclic caryophyllene.

J. J. S.

Philippine Terpenes and Essential Oils. IV. RAYMOND F. BACON (*Philippine J. Sci.*, 1910, 5, 257—265. Compare Abstr., 1909, i, 658).—The volatile oils from a number of plants indigenous to, or cultivated in, the Philippines are described.

Cinnamomum mindanaense bark furnishes a yellow oil, D_{30}^{30} 0·960, n_D^{30} 1·5300, α_D^{30} +7·9°, containing 60% of an aldehyde, and having a strong odour of cinnamon. *Canarium villosum* yields an oleo-resin, which on distillation furnishes about 11% of oil, distilling mainly between 154° and 180°, and containing pinene and dipentene. Native grown ginger-root furnished 0·072% of a pale yellow oil, D_{30}^{30} 0·8850, n_D^{30} 1·4830, α_D^{30} +5·9°, and saponification number 14; this had an odour similar to that of orange-peel oil, and was completely soluble in two or more volumes of 90% alcohol. *Ocimum sanctum* leaves gave 0·6% of greenish-coloured oil, having α_D^{30} 0, n_D^{30} 1·5070, D_{30}^{30} 0·952, and saponification value 2·8. It had an anise-like odour, and the fraction boiling at

85—95°/9 mm. gave homoanisic acid on oxidation. *Curcuma Zedoaria* roots furnished 0·065 to 0·25% of brown oil, D_4^{30} 0·933, n_D^{30} 1·4920 to 1·5070, α_D^{30} + 1°10′, saponification value 2, and soluble in two or more volumes of 80% alcohol. The oil boiled from 60° to 166°/7 mm., and the higher fractions contained a sesquiterpene alcohol, D_{30}^{30} 1·01, m. p. 67°, b. p. 160°/7 mm., which appears to be the chief odoriferous constituent of the oil, and to belong to the tricyclic group. It gave a deep red colour with sulphuric acid. Turmeric roots furnished a brownish-coloured oil, having D_{30}^{30} 0·390, n_D^{30} 1·5030, α_D^{30} + 8·6°, ester number 81, and miscible with 75% or stronger alcohol in all proportions (compare Rupe, Luksch, and Steinbach, Abstr., 1909, i, 598). The yellow flowers of *Michelia champaca* furnished 0·2% of oil, which when kept, deposited (1) a crystalline solid, (2) an amorphous solid. The residual brown oil so obtained had D_{30}^{30} 0·9543—1·020, n_D^{30} 1·4550—1·4830, saponification number 160—180; that having the higher constants had the finer odour. It is considered likely that the reputed Manila champaca oils examined by previous investigators were not derived wholly from champaca flowers. T. A. H.

Essential Oil of Spanish Wild Marjoram. BERNABÉ DORRONSORO (*Anal. Fis. Quim.*, 1910, 8, 315—328).—Spanish wild marjoram (*Mejorana silvestre, Thymus Mastichina*, L.) is distilled largely in the south and centre of Spain. Authentic samples of the oil taken in the years 1898–1909 gave values D_{15}^{20} 0·907—0·945, n_D^{23} 1·4630—1·4654, and α_D^{25} varying from −1°40′ to +9°20′ (200 mm. tube).

The saponification value of the oil had a range 12·7—18·5 with samples taken during the years 1898–1909; the esters calculated as linalyl acetate ranged from 4·44—6·47%; the acetylation number ranged from 29·2—45·6, and the alcohol, calculated as $C_{10}H_{18}O$, varied from 8·20—13·0. The analysis of a 5 kilogram sample gave the following result: *d*-pinene, 7—8%; cineol or eucalyptol, 64—72%; phenols, less than 0·1%; ketones, less than 0·1%; esters (as linalyl acetate), 4·44—6·47%, and free alcohols (linalool), 8·2—14·1%.

The remarkable point with regard to this oil is the production from a species of *Thymus* of a high proportion of cineol and the entire absence of thymol, cineolic acid, and methylheptenone; the oxidation products of cineol are also absent. W. A. D.

So-called Crystalline Chlorophyll—a Mixture. M. TSVETT (*Ber.*, 1910, 43, 3139—3141).—The green crystals of chlorophyll discovered by Borodin, and recently investigated by Willstätter, have been regarded (Tsvett, Abstr., 1908, i, 669) either as a compound of the genuine chlorophyllins with possibly a third substance, or as an isomorphous mixture of two chlorophyllin derivatives. By means of the adsorption analysis of crystalline chlorophyll, dissolved in ether and diluted with ten volumes of light petroleum, the chromatogram is proved to show two zones—a superior greenish-yellow and an inferior greenish-blue. Accordingly, crystalline metachlorophyllin is an isomorphous mixture of α- and β-metachlorophyllins. E. F. A.

Di-ω-hydroxy-2 : 5-dimethylfuran. JAN J. BLANKSMA (*Rec. trav. chim.*, 1910, **29**, 403—406).—Although hexoses yield δω-hydroxymethylfurfuraldehyde when heated with oxalic acid, the author found that hexonic acids and the hexitols do not give di-ω-hydroxy-2 : 5-dimethylfuran under similar conditions. This substance may, however, be prepared by the action of sodium hydroxide on hydroxymethylfurfuraldehyde, hydroxymethylpyromucic acid being formed at the same time.

The crystals of *di-ω-hydroxy-2 : 5-dimethylfuran* are colourless, m. p. 80°; the *diacetyl* derivative forms colourless crystals, m. p. 64°.

The *semicarbazone* of hydroxymethylfurfuraldehyde crystallises in large, colourless crystals, m. p. 192°; its p-*bromophenylhydrazone* forms pale yellow crystals, m. p. 142°, which darken when exposed to sunlight. N. C.

Cyclic Sulphides. JULIUS VON BRAUN (*Ber.*, 1910, **43**, 3220—3226. Compare Abstr., 1910, i, 274).—The action of potassium sulphide on αζ-di-iodohexane yields only a very small quantity of hexamethylene sulphide, $(CH_2)_6S$, so that the tendency to the formation of the cyclic sulphides, $(CH_2)_nS$, diminishes progressively as n increases from 4 to 6.

If, however, two adjacent carbon atoms of a benzene ring are included in the chain, the formation of a cyclic sulphide containing a 6-membered ring takes place very readily; thus tetrahydrobenzthiopyran is produced in almost quantitative yield from *o*-ω-chloropropylthiophenol, $C_6H_4<\begin{matrix}[CH_2]_3Cl\\SH\end{matrix}$.

It has been shown previously by the author (Abstr., 1910, i, 821) that the action of αζ-di-iodohexane on amines is accompanied by an isomerisation of the hexamethylene chain, the compounds produced containing the α-pipecoline ring and not a 7-membered ring. In order to determine if a similar transformation occurs in the formation of cyclic sulphides, the interaction of potassium sulphide and αδ-di-iodopentane has been investigated. The cyclic sulphide so obtained is different from that produced by the action of potassium sulphide on αε-di-iodopentane, so that no isomerisation of the pentamethylene chain has taken place in the latter reaction.

αδ-Di-iodopentane reacts vigorously with concentrated aqueous potassium sulphide in the presence of a little alcohol, yielding a *compound*, $C_{11}H_{18}O$, b. p. 229—230°, 122°/24 mm., and 2-*methyltetrahydrothiophen*, $\begin{matrix}CH_2\cdot CHMe\\|\qquad\quad\\CH_2—CH_2\end{matrix}>S$, b. p. 134°, a colourless liquid with a disagreeable odour, which yields a *methiodide*, crystallising in long, stout prisms, subliming at 172—173°, and transformed when kept in a desiccator into an amorphous, horny mass; the *platinichloride*, $(C_5H_{10}SMe)_2PtCl_6$, crystallises in reddish-yellow leaflets, m. p. 197° (decomp.).

The cyclic *sulphide*, $C_6H_{12}S$, is produced in a yield of 6% by the interaction of potassium sulphide and αζ-di-iodohexane in aqueous-alcoholic solution. It is a colourless oil, and gives a *methiodide*, crystallising in colourless needles, m. p 147°.

The *platinichloride* crystallises from water in reddish-yellow leaflets, m. p. 193°.

The main product of the action of potassium sulphide on $\alpha\zeta$-di-iodohexane forms an *oil*, which solidifies on cooling, and probably consists of $I\cdot[CH_2]_6\cdot(S\cdot[CH_2]_6)_n\cdot S\cdot[CH_2]_6\cdot I$.

Thiochroman (*tetrahydrobenzthiopyran*), $C_6H_4<\begin{matrix}S\text{—}CH_2\\ \phantom{S\text{—}}| \\ CH_2\cdot CH_2\end{matrix}$, b. p. 128—130°/15 mm., is obtained as an almost odourless, pale yellow oil by the addition of potassium xanthate to a diazotised solution of *o*-ω-chloropropylaniline, slowly heating the *diazoxanthate*,

$$Cl\cdot[CH_2]_3\cdot C_6H_4\cdot N_2\cdot S\cdot CS\cdot OEt,$$

thus produced to 70°, and boiling the resulting dark-coloured *oil*, probably $Cl\cdot[CH_2]_3\cdot C_6H_4\cdot S\cdot CS\cdot OEt$, with alkali in aqueous-alcoholic solution. It does not react readily with methyl iodide, and on treatment with methyl sulphate yields a dark viscid, liquid *additive product*, which solidifies after several weeks' keeping.

Thiochromansulphone, $C_6H_4<\begin{matrix}SO_2\text{—}CH_2\\ \phantom{SO_2\text{—}}| \\ CH_2\cdot CH_2\end{matrix}$, white crystals, m. p. 88·5°, is produced by oxidising thiochroman with potassium permanganate in aqueous solution. F. B.

Ephedrine and ψ-Ephedrine. FRANZ WILHELM CALLIESS (*Apoth. Zeit.*, 1910, **25**, 677—678).—Schmidt has shown previously (Abstr., 1908, i, 452) that when either of these bases is treated with hydrochloric acid at 100°, an equilibrium mixture of both is formed. It is now shown that ephedrine on acetylation is completely converted into ψ-ephedrine. The hydrochloride of either base on treatment with acetic anhydride yields an *acetyl* derivative, $C_{10}H_{14}ONAc,HCl$, m. p. 175°, $[\alpha]_D$ +96·7°, crystallising in colourless columns or tablets, which on hydrolysis by hydrochloric acid furnishes ψ-ephedrine. The *platinichloride* of the acetyl derivative, m. p. 184°, and the *aurichloride*, m. p. 165°, were prepared. T. A. H.

Components of Opium. LEOPOLD VAN ITALLIE and MAX KERBOSCH (*Arch. Pharm.*, 1910, **248**, 609—613).—Samples of opium from the Levant, India, China, America, France, Persia, and Egypt have been examined for the presence of morphine, narcotine, papaverine, thebaine, codeine, and narceine, the six commonest of the twenty-odd alkaloids in opium. The six alkaloids have been found in all of the samples except in the Indian opiums from Bengal, Patna, and Benares; these three do not contain papaverine. A reason for this peculiarity is being sought; it is not to be explained by difference in origin, because, as far as information is available, Bengal, Patna, and Benares opiums are obtained from the same plant, *Papaver somniferum* var. *album*, as Persian, Egyptian, Levantine, and other Indian opiums. C. S.

Action of Hydrogen Peroxide on Thebaine, Morphine, and their Ethers. MARTIN FREUND and EDMUND SPEYER (*Ber.*, 1910, **43**, 3310—3314).—When heated on the water-bath with 30%

hydrogen peroxide, thebaine, morphine, codeine, and dionine are converted into substances which are regarded as amine-oxides, since they are re-converted into the original alkaloids by sulphurous acid. They are characterised, however, by their stability towards acidified potassium iodide, and by their very slight physiological activity. *Thebaine oxide*, $C_{19}H_{21}O_4N$, m. p. about 80°, forms a *hydrochloride*, m. p. 238—239° (decomp.), colourless needles. *Morphine oxide*, $C_{17}H_{19}O_4N$, m. p. 274—275°, prismatic crystals, forms a *nitrate*, $C_{17}H_{19}O_4N,HNO_3,1\frac{1}{2}H_2O$, m. p. 206—208°, which loses water when heated, yielding a *substance*, $C_{34}H_{38}O_{13}N_4$, from which the hydrated nitrate is regenerated by crystallisation from water. *Codeine oxide*, $C_{18}H_{21}O_4N$, m. p. 230—231°, rectangular plates, forms a *nitrate*, m. p. 187°, and a *hydrobromide*, m. p. 196°. *Dionine oxide*, $C_{19}H_{23}O_4N$, m. p. 220—221°, felted needles, forms a *hydriodide*, which crystallises in elongated plates. C. S.

Narcotine and Hydrastine. PAUL RABE and ANDREW MCMILLAN (*Annalen*, 1910, **377**, 223—258).—A résumé of the development of the constitutional formulæ of hydrastine, narcotine, and narceine is given.

A proof is given that in Rabe's nornarceine (Abstr., 1907, i, 790) the carbonyl group is attached directly to the benzene nucleus; hence the same arrangement obtains in narceine itself (compare Freund and Oppenheim, Abstr., 1909, i, 410). The crude oximino-compound, m. p. 167—169°, obtained by treating nornarceine with alcoholic sodium ethoxide and ethyl nitrite, is suspended in chloroform at 0°, and converted by phosphorus pentachloride into hemipinic acid and 2-*cyano*-3-*methoxy*-4 : 5-*methylenedioxy*-1-*β*-*methylaminoethylbenzene*,

$$CH_2O_2\!:\!C_6H(OMe)(CN)\cdot CH_2\cdot CH_2\cdot NHMe,$$

m. p. 61°, which forms a *hydrochloride*, m. p. 206—207° (decomp.), *picrate*, m. p. 168°, *picrolonate*, decomp. 232°, and a methiodide, m. p. 226°, identical with Freund and Oppenheim's compound (*loc. cit.*). In a similar manner, methylhydrasteine forms an *oximino*-compound,

$$C_{22}H_{24}O_8N_2,$$

m. p. 189—190°, which is converted by phosphorus pentachloride into hemipinic acid and 2-*cyano*-4 : 5-*methylenedioxy*-1-*β*-*dimethylaminoethylbenzene*, $CH_2O_2\!:\!C_6H_2(CN)\cdot CH_2\cdot CH_2\cdot NMe_2$, which forms a *picrate*, m. p. 188—189°, and *methiodide*, m. p. 260° (decomp.). The authors have little doubt that Beckett and Wright's oxynarcotine is identical with nornarceine; the substances have the same composition, $C_{22}H_{25}O_8N$, the same crystalline form, and behave alike as regards their solubility in organic solvents and in alkali hydroxides, and their insolubility in alkali carbonates.

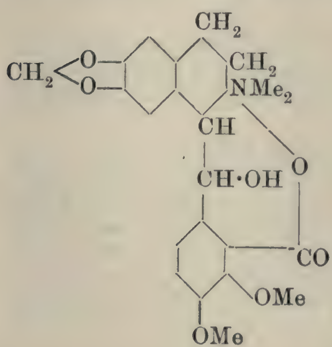
In the authors' opinion, gnoscopine is not a natural product of the plant, but is produced by racemisation of narcotine during its isolation from opium. Although the different behaviour of narcotine and gnoscopine towards acids and alkalis might well lead to the belief that they are differently constituted, there can be no doubt that the latter is *r*-narcotine (Abstr., 1910, i, 335). Since hot dilute acetic acid converts gnoscopine into cotarnine, meconine, and nornarceine (Abstr., 1907, i,

790), the changes produced by heating *l*-narcotine with dilute acetic acid are represented by the diagram :

$$\begin{array}{ccccc} & \swarrow & l\text{-Narcotine} & \searrow & \\ \text{Nornarceine} & & \downarrow & & \text{Cotarnine} + \text{Meconine.} \\ & \nwarrow & \text{Gnoscopine} & \nearrow & \end{array}$$

Similar changes are effected by heating *l*-narcotine with aqueous barium hydroxide or with dilute alcohol; hot 10% sulphuric acid, however, only slowly decomposes *l*-narcotine into cotarnine and meconine, the formation of gnoscopine and nornarceine not being observed.

The behaviour of the quaternary ammonium derivatives of hydrastine and narcotine has been examined. The aqueous solution obtained by treating hydrastine methiodide (or, better, methochloride) with moist silver oxide deposits a substance, m. p. 242°, which receives, in preference to Freund's formula, the annexed constitution of an oxybetaine on account of its neutral character and inability to form a methiodide. When hydrastine methiodide or methochloride is treated with aqueous alkalis instead of with silver oxide, it is converted into methylhydrastine. Both this substance and the oxybetaine are unstable, and change into the basic keto-acid, methylhydrasteine. In the decomposition of hydrastine methiodide or of the hydroxide, no trace of meconine or of methylhydrastinine has been observed; even when the methochloride is boiled with dilute acetic acid, meconine is not formed, only the oxybetaine, m. p. 242°.



The quaternary ammonium compounds of narcotine behave in a similar manner. When the methochloride is treated with water and silver oxide, an alkaline solution is obtained, which, by keeping, deposits narceine and becomes neutral; it then contains an oxybetaine, which, however, cannot be isolated, all experiments with this object resulting in its transformation into narceine. When narcotine methochloride is treated with aqueous sodium hydroxide, it is converted into methylnarcotine (*methiodide*, $C_{23}H_{25}O_7N,MeI$, m. p. about 260°), which is changed by methyl iodide and methyl alcohol into the methiodide of narceine methyl ester by addition of methyl iodide, opening of the lactone ring, and addition of methyl alcohol. Methylnarcotine is converted with great ease, even by boiling water, into the basic keto-acid, narceine.

An important result of the preceding experiments is the following. Hydrastine and narcotine and their derivatives, containing tervalent nitrogen, experience a rupture of the carbon chain by hydrolytic decomposition, and yield meconine, cotarnine, etc. Derivatives containing quinquevalent nitrogen, however, retain the carbon chain

unbroken, but yield basic keto-acids by opening of the *iso*quinoline ring. C. S.

Vegetable Betaines and Stachydrine. ERNST SCHULZE and G. TRIER (*Zeitsch. physiol. Chem.*, 1910, **69**, 326—328. Compare Abstr., 1909, i, 323).—A reply to Engeland. Purely polemical. J. J. S.

Conversion of Hydroxymethyleneacetophenone into Benzoylpyruvic Acid and Some New Derivatives. OTTO MUMM and GEORG MÜNCHMEYER (*Ber.*, 1910, **43**, 3335—3345).—The iminochlorides of aromatic acid-anilides undergo displacement of the halogen by the cyano-group by treatment with aqueous potassium cyanide, and react with the sodium salts of organic acids to form diacylanilides (Abstr., 1910, i, 311). The formation of diacylamines from the methiodides of 5-alkyl*iso*oxazoles and the sodium salts of organic acids is probably due to the intermediate change of the *iso*oxazole to an imino-iodide, thus:

$$\begin{matrix} CPh—O \\ \| \\ CH{\cdot}CH \end{matrix}\!\!>\!N,MeI \longrightarrow CH_2Bz{\cdot}CI{:}NMe,$$

which is then converted into the diacylamine, $CH_2Bz{\cdot}CO{\cdot}NMeX$ (X = acyl). If this is so, the methiodides of 5-alkyl*iso*oxazoles should react with potassium cyanide in accordance with the equation $\begin{matrix} CPh—O \\ \| \\ CH{\cdot}CH \end{matrix}\!\!>\!N,MeI + KCN = KI + CH_2Bz{\cdot}C(CN){:}NMe$. This is the case (in practice, the more easily obtainable methosulphate is employed), the reaction thus furnishing a method of converting hydroxymethyleneacetophenone through the *iso*oxazole into benzoylpyruvic acid.

In Claisen's method of preparing hydroxymethyleneacetophenone, the yield is increased by 50% by using $1\frac{1}{2}$ mols. of ethyl formate instead of 1 mol. 5-Phenyl*iso*oxazole, obtained from hydroxymethyleneacetophenone by Zöpfchen's process, is treated with an equal molecular quantity of methyl sulphate, and the resulting additive compound treated with aqueous potassium cyanide in the cold, whereby *α-methylimino-β-benzoylpropiontrile*, $CH_2Bz{\cdot}C({:}NMe){\cdot}CN$, m. p. 128°, yellow needles, is obtained. The nitrile is converted into ethyl benzoylpyruvate by equal parts of concentrated hydrochloric acid and alcohol, into benzoylpyruvic acid by boiling dilute hydrochloric acid, into *α-methylimino-β-benzoylpropionic acid*, $CH_2Bz{\cdot}C({:}NMe){\cdot}CO_2H$, m. p. 163°, yellow needles, by cold concentrated hydrochloric acid, and into *benzoylpyruvamide*, $CH_2Bz{\cdot}CO{\cdot}CO{\cdot}NH_2$, m. p. 138° (decomp.), by cold dilute hydrochloric acid; the amide develops a dark red coloration with ferric chloride, and by treatment with sodium hydroxide or sodium carbonate forms a *sodium* derivative which decomposes after a long time, yielding acetophenone. With a methyl-alcoholic solution of sodium methoxide or potassium hydroxide, the nitrile yields methyl methyliminobenzoylacetate. C. S.

2:3-Diketo-5-phenylpyrroline, a Uninuclear Analogue of Isatin. OTTO MUMM and GEORG MÜNCHMEYER (*Ber.*, 1910, **43**, 3345—3359).—By passing hydrogen chloride into a well-cooled paste

of α-methylimino-β-benzoylpropionitrile (preceding abstract) in methyl alcohol, a dark red substance, *2-keto-3-methylimino-5-phenylpyrroline hydrochloride*, $\begin{matrix}CPh{:}CH \\ | \\ NH\cdot CO\end{matrix}\!\!>C{:}NMe,HCl$ (see below for constitution), is obtained, which crystallises with $2H_2O$ (m. p. about 114°) or with H_2O (m. p. 147—150°), according to the method of isolation; the *picrate*, $C_{17}H_{13}O_8N_5$, m. p. 178°, is anhydrous. By treatment with cold water it is converted quantitatively into methylamine hydrochloride and 2 : 3-*diketo-5-phenylpyrroline*, $NH<\begin{matrix}CO-CO \\ CPh{:}CH\end{matrix}$, m. p. 210°, which crystallises in brick-red leaflets. The proof that these two substances are cyclic compounds, not derivatives of benzoylpyruvic acid, rests on their colour, the absence of the ferric chloride reaction, and the analogy of the latter compound to isatin. The formation of the former is explained by the intermediate production of an iminoether, $CH_2Bz\cdot C({:}NMe)\cdot C({:}NH)\cdot OMe$, since the substance is only produced in alcoholic solution. 2 : 3-Diketo-5-phenylpyrroline forms an *oxime*, yellow plates, decomp. 213° (from which a *dioxime*, m. p. 181—182°, can be obtained, the absence of colour of which renders it doubtful whether the compound has a cyclic structure), a *phenylhydrazone*, yellowish-red needles, m. p. 240° (decomp.), and a p-*nitrophenylhydrazone*, dark red needles, m. p. about 285° (decomp.); the production of the same three substances from 2-keto-3-methylimino-5-phenylpyrroline hydrochloride determines the presence of the oximino-group in position 3. Diketophenylpyrroline forms colourless solutions in aqueous sulphurous acid or sodium hydrogen sulphite; an impure additive compound can be isolated in the latter case. Diketophenylpyrroline shows its analogy to isatin, not only by responding to the indophenin reaction, but also by its behaviour with cold sodium hydroxide, whereby a bluish-violet solution is obtained, the colour of which disappears after a few minutes, and, after acidification, γ-*iminobenzoylpyruvic acid*, $NH{:}CPh\cdot CH_2\cdot CO\cdot CO_2H$, m. p. 161°, is formed, which differs from the isomeric benzoylpyruvamide (*loc. cit.*) in forming a stable *sodium* salt, and in developing an orange-red coloration with ferric chloride. γ-*Iminobenzoylpyruvamide*,

$$NH{:}CPh\cdot CH_2\cdot CO\cdot CO\cdot NH_2,$$

m. p. 158—159°, is obtained by treating diketophenylpyrroline with concentrated ammonia at the ordinary temperature; it has neither acidic nor basic properties, develops an orange-red coloration with ferric chloride, and, like the γ-imino-acid itself, is converted into benzoylpyruvic acid by evaporating its solution in 50% alcohol containing a little hydrochloric acid.

By treatment with cold aqueous sodium hydrogen carbonate, 2-keto-3-methylimino-5-phenylpyrroline hydrochloride is converted into a *hydroxide*, m. p. 110—120°, which, on account of its faint greenish-yellow colour and feebly basic character, receives the constitution of a ψ-base, $NHMe\cdot C(OH)<\begin{matrix}CH{:}CPh \\ | \\ CO-NH\end{matrix}$; it is characterised by forming equally intensely coloured salts with either sodium hydroxide or with hydrochloric acid. These salts are therefore constituted alike; the

sodium salt receives the constitution $NMe{:}C{<}\begin{matrix}CH{=\!=}CPh \\ C(ONa){:}N\end{matrix}$, the hydrochloride that given above. C. S.

Action of Pyridine on Iridiodisulphates. MARCEL DELÉPINE (*Compt. rend.*, 1910, **151**, 878—880. Compare Abstr., 1909, ii, 408).—A solution of ammonium iridiodisulphate does not lose its green colour when mixed with pyridine, but a change takes place, especially on boiling the liquid. The solution then contains *pyridino-iridiodisulphuric acid*, $OHIr(C_5H_5N)(SO_4H)_2$, and gives crystalline precipitates with salts of sodium, potassium, rubidium, cæsium, thallium, silver, strontium, barium, lead, and chromium. Salts have been analysed having the following formulæ, in which R represents the group $[OH{\cdot}(C_5H_5N)Ir(SO_4)_2]''$:—$R(NH_4)_{1\cdot5},5H_2O$, $RNa_{4/3}H_{2/3},1{\cdot}5H_2O$, $RK_{4/3}H_{2/3},2H_2O$, $RBa_{2/3}H_{2/3},3H_2O$, $RAg_{4/3}H_{2/3},H_2O$. The salts are deep green and form olive-green solutions. The barium salt is very sparingly soluble, and owing to its crystalline form can be used to characterise the acid or its salts. W. O. W.

[Constitution of Benzoylanthranil.] GUSTAV HELLER (*Ber.*, 1910, **43**, 3365).—Mumm and Hesse regard the constitution, $C_6H_4{<}\begin{matrix}-N{:}CPh \\ CO{\cdot}O\end{matrix}$, of benzoylanthranil as being definitely proved by the formation of benzoylanthranil and aniline by the interaction of anthranilic acid and benzanilideiminochloride (Abstr., 1910, i, 770). The author fails to see why the reaction cannot be explained by the following scheme, which leads to the constitution of benzoylanthranil proved by his own experiments: $CO_2H{\cdot}C_6H_4{\cdot}NH_2 + CClPh{:}NPh \longrightarrow C_6H_4{<}\begin{matrix}NH{\cdot}CPh{:}NPh \\ CO_2H\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}N{\cdot}COPh \\ CO\end{matrix} + NH_2Ph.$ C. S.

Quinoline-5-carboxylic Acid. I. ZYG. VON JAKUBOWSKI (*Ber.*, 1910, **43**, 3026—3032. Compare Abstr., 1909, i, 264).—To prepare quinoline-5-carboxylic acid, *o*-amino-*p*-toluonitrile is condensed with glycerol in presence of arsenic acid to 5-methylquinolyl-8-carboxylic acid. On distillation with calcium hydroxide, 5-methylquinoline is obtained, and this is oxidised to the 5-carboxylic acid, which is similar to the ψ-quinoline-*ana*-carboxylic acid described by Lellmann and Alt (compare Abstr., 1887, 502, 737, 973; 1888, 296, 499).

5-*Methylquinoline*-8-*carboxylic acid*, $C_9NH_6Me{\cdot}CO_2H$, crystallises in small needles of silvery lustre, m. p. 173—174°. The *ammonium*, *calcium*, and *copper* salts are described: the *hydrochloride* forms concentrically grouped needles; the *nitrate*, long needles of silky lustre; the *picrate*, slender, yellow needles, m. p. 205—207°; the *platinichloride*, pale yellow, concentrically intergrown needles, and the *dichromate*, orange rods.

By the distillation of 5-methylquinoline-8-carboxylic acid with calcium oxide, a by-product is formed, which crystallises in colourless needles, m. p. 200—202°. This is probably a new dimethyldiquinonyl; it is not identical with 5 : 5′-dimethyl-8 : 8′-diquinonyl. The main product

is 5-*methylquinoline*, a colourless liquid, b. p. 253—255°/735 mm. The *picrate* forms light yellow plates, which soften at 200°, m. p. 210—213°. The *mercurichloride* forms small, colourless needles; the *platinichloride*, bright orange needles; the *methiodide*, yellow, silky needles, m. p. 105°.

On oxidation with a mixture of chromic and sulphuric acids, quinoline-5-carboxylic acid is obtained. E. F. A.

Aromatic Hydrazines. VIII. Oxidation of Diphenylhydrazine. HEINRICH WIELAND and ERNST WECKER (*Ber.*, 1910, **43**, 3260—3271).—The reddish-violet dye prepared by the action of acid oxidising agents, more particularly of hypochlorous acid, on diphenylhydrazine (compare E. Fischer, Abstr., 1878, 313) is the hydrochloride of quinoneanildiphenylhydrazone,

$$NPh\colon C_6H_4\colon N\cdot NPh_2,HCl.$$

This constitution follows from: (*a*) analysis; (*b*) the products of reduction, namely, diphenylamine and *p*-aminodiphenylamine; (*c*) its oxidation value as determined by Willstätter and Piccard's method (*Ber.*, 1908, **41**, 1474). Attempts to synthesise the dye by the condensation of quinoneanil with diphenylhydrazine hydrochloride showed that the chief products were tetraphenyltetrazen and *p*-hydroxydiphenyl, together with a brilliant bluish-violet dye, which on reduction gave diphenylamine and an unknown *p*-hydroxyaminodiphenylamine. In the formation of this bluish-violet dye, an additive product is probably formed, which is oxidised by the excess of quinoneanil to an orthoquinonoid compound, $NPh_2\cdot N\colon C<\begin{matrix}C(\colon NPh)\text{—}CH \\ CH\colon C(OH)\cdot CH\end{matrix}$, the hydrochloride of which is the dye.

It is shown that in the formation of the red dye, diphenylhydroxylamine is probably an intermediate product, which condenses with the diphenylhydrazine, yielding the triazo-derivative, $NH(NPh_2)_2$. This then undergoes a type of molecular rearrangement resembling that of diazoamino-compounds, thus yielding $NHPh\cdot C_6H_4\cdot NH\cdot NPh_2$, which is oxidised to the dye base, $NPh\colon C_6H_4\colon N\cdot NPh_2$. Further confirmation of this view is afforded by the fact that tetraphenylhydrazine, which is known to be readily hydrolysed to diphenylamine and diphenylhydroxylamine (Wieland, Abstr., 1907, i, 1076; 1908, i, 1014), reacts with a glacial acetic acid solution of diphenylhydrazine at 55—60°, yielding the red dye. Di-*p*-tolylhydrazine does not yield a dye when oxidised, but when warmed with glacial acetic acid and tetraphenylhydrazine gives a red dye. The formation of a dye cannot therefore be merely due to the oxidising action of the tetraphenylhydrazine on the diphenyl or di-*p*-tolylhydrazine, but must be due to the hydrolysis to diphenylhydroxylamine, which then condenses with the secondary hydrazine.

p-Substituted tetraphenylhydrazines do not yield dyes with di-*p*-tolylhydrazine.

Quinoneanildiphenylhydrazone hydrochloride, $C_{24}H_{19}N_3,HCl$, is deposited in glistening, bronzy-green crystals, m. p. 147°, when light petroleum is added to its alcoholic ethereal solution. The yield is poor, and the method of purification is tedious. Both the solid and its

solutions are stable. It dyes cotton mordanted with tannin a brilliant violet-red. Its solution in concentrated sulphuric acid has a greenish-blue colour, but turns reddish-violet when diluted. When boiled for some time with mineral acids, it yields small amounts of diphenylamine, and when shaken with 20% sulphuric acid and lead peroxide yields quinone. The *base* has only been obtained in the form of an amorphous, reddish-brown powder. The majority of its salts and double salts are sparingly soluble in water, and do not crystallise well. Solutions do not give any characteristic absorption bands.

p-Methyl- and *p*-methoxy-diphenylhydrazine give similar dyes, but the di-*p*-tolyl and dianisyl compounds do not.

p-*Hydroxy*-o-*quinoneanildiphenylhydrazone hydrochloride*,

$$C_{24}H_{19}ON_3,HCl,$$

obtained by condensing quinoneanil with diphenylhydrazine hydrochloride, is more soluble in water than the red dye, and the solutions have more of a bluish tint. The *base* has a fiery brownish-red colour, and is amphoteric; it dissolves in both acids and alkalis, giving brilliant violet solutions. When reduced with stannous chloride, it yields p-*hydroxy*-o-*aminodiphenylamine*, $NHPh\cdot C_6H_3(OH)\cdot NH_2$, which crystallises from alcohol, has m. p. 170—171°, and dissolves in both acids and alkalis.

These solutions are readily oxidised to blue amphoteric dyes.

J. J. S.

Phenylhydrazones of Dextrose. ROBERT BEHREND and WILLY REINSBERG (*Annalen*, 1910, 377, 189—220).—The phenylhydrazone of dextrose, like dextrose itself, exists in two forms, which exhibit birotation, and, when dissolved, give ultimately identical solutions by the formation of the same equilibrium mixture. The theory advanced by Behrend and Lohr (Abstr., 1908, i, 765) that one of these dextrose-phenylhydrazones is a true hydrazone,

$$CH_2(OH)\cdot[CH(OH)]_4\cdot CH{:}N\cdot NHPh,$$

and the other a hydrazide,

$$CH_2(OH)\cdot CH(OH)\cdot\overbrace{CH\cdot[CH(OH)]_2\cdot CH}^{O}\cdot NH\cdot NHPh,$$

has been proved in the following ways.

By treatment with acetic anhydride in pyridine, dextrose-β-phenylhydrazone yields an amorphous acetate, whilst dextrose-α-phenylhydrazone gives a crystalline acetate, m. p. 152—153°, together with an amorphous acetate (Hofmann, Abstr., 1909, i, 519). (The author shows that these are penta-acetates, and that the last-mentioned, amorphous acetate is a mixture of the other two.) True hydrazones yield *N*-acetyl derivatives only with difficulty, and are not attacked by acetic anhydride in cold pyridine. Since the crystalline dextrose-α-phenylhydrazone penta-acetate, by treatment with aqueous-alcoholic potassium hydroxide and benzaldehyde, yields acetylphenylbenzylidenehydrazine, whilst the amorphous dextrose-β-phenylhydrazone penta-acetate under similar conditions gives phenylbenzylidenehydrazine, it follows that dextrose-α-phenylhydrazone penta-acetate contains an acetyl group attached to a nitrogen atom and is therefore produced from a hydrazide, and that dextrose-β-phenylhydrazone penta-acetate

does not contain an acetylated nitrogen atom and is therefore produced from a true hydrazone. Dextrose-α-phenylhydrazone and dextrose β-phenylhydrazone have the hydrazide and the hydrazone constitution respectively. This conclusion is supported by the fact that dextrose-α-phenylhydrazone penta-acetate yields α-acetylphenylhydrazine by hydrolysis with 5% hydrochloric acid, whilst the β-isomeride resinifies.

Another proof of the theory is furnished by condensing dextrose with α-acetylphenylhydrazine in warm alcohol containing a little acetic acid. The condensation product is a syrup from which a crystalline substance cannot be isolated, but from which, after treatment with acetic anhydride in cold pyridine, dextrose-α-phenylhydrazone penta-acetate has been obtained; this acetate, therefore, certainly has an acetyl group attached to a nitrogen atom. If the original syrupy condensation product contains a true hydrazone, there must still be five hydroxyl groups in its dextrose nucleus capable of acetylation. The fact that the product obtained by acetylating the syrup in pyridine contains, in addition to dextrose-α-phenylhydrazone penta-acetate, a *hexa-acetate*, shows that a true hydrazone must be present in the syrupy mixture of the dextroseacetylphenylhydrazines. This hexa-acetate, $C_{24}H_{30}O_{11}N_2$, which is separated from the accompanying penta-acetate by solution in ether, is an amorphous powder having $[\alpha]_D + 143·1°$ in pyridine and $137·9°$ in benzene without mutarotation.

Dextrose-α-phenylhydrazone penta-acetate, obtained by Hofmann's method (*loc. cit.*), has m. p. 152—153°, and $[\alpha]_D + 11·97°$ in pyridine.

The acetate separated by ether from the crude acetylated product partly melts at 130°, resolidifies, and then has m. p. 150—152°; if after being heated to 150° the acetate is recrystallised from alcohol, it has m. p. 152° without previous fusion at 130°. When the crude acetylated product is treated with an amount of ether insufficient for complete solution, the residual sparingly soluble substance has m. p. 110°, then resolidifies, and changes into the acetate, m. p. 152—153°. The latter can be converted into the substance having m. p. 110° by gently boiling its solution in ether. In pyridine the two substances have the same specific rotation, $[\alpha]_D + 17·5°$, without mutarotation. The relation between the two substances is not yet settled; it appears to be due to polymorphism.

α-Acetylphenylhydrazine can be obtained in 76·84% yield by hydrolysing β-formyl-α-acetylphenylhydrazine with concentrated hydrochloric acid; when the hydrolysis is effected by aqueous potassium hydroxide, β-formylphenylhydrazine is produced. C. S.

1-Benzoylphenyl-3-methyl-5-pyrazolone. HENRY A. TORREY and H. R. RAFSKY (*J. Amer. Chem. Soc.*, 1910, **32**, 11, 1489—1492).—The pyrazolone was prepared by Michael's method from the hydrochloride of *p*-hydrazinobenzophenone and acetoacetic acid. Modifications were introduced in the preparation of *p*-aminobenzophenone (Döbner, *Annalen*, 1881, **210**, 267) and of *p*-hydrazinobenzophenone (Ruhemann and Blackman, Trans., 1889, i, 613).

1-*Benzoylphenyl-3-methyl-5-pyrazolone*, $\begin{matrix}CH_2·CO\\|\\CMe{=}N\end{matrix}\!\!>\!N·C_6H_4Bz$, forms

brownish-yellow crystals, m. p. 170—171°. It gives a white, flocculent precipitate with silver nitrate, and does not reduce Fehling's solution. Its *hydrochloride* was obtained as a pale brown powder, m. p. 196° (decomp.), turning dark at 180°. A small amount of 1-*benzoylphenyl-2 : 3-dimethyl-5-pyrazolone* was obtained, m. p. 125°. N. C.

Oxidoanhydro-compounds. I. STEFAN VON NIEMENTOWSKI (*Ber.*, 1910, **43**, 3012—3026).—The two first members of the series of oxyanhydro-compounds, namely, benziminazole oxide and 2-methylbenziminazole oxide, were hitherto unknown; they have now been obtained by reduction of *o*-nitroformanilide and *o*-nitroacetanilide with ammonium sulphide in alcoholic solution.

Benziminazole oxide, when treated with benzoyl chloride and sodium hydroxide, undergoes intramolecular rearrangement to *o*-phenylenecarbamide, $C_6H_4<{NH \atop NH}>CO$, m. p. 310°. The same rearrangement is observed on heating with hydrochloric acid in sealed tubes at 200°, on fusion with potassium hydroxide, and on heating with zinc dust at 230°. Apparently, the carbamide is the stable isomeride; it has not been found possible to convert it into oxidobenziminazole.

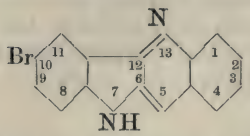
o-Nitroformanilide is prepared by heating *o*-nitroaniline with anhydrous formic acid. The reduction product, *benziminazole oxide*, $O<{N—C_6H_4 \atop CH·NH}$, forms colourless needles, m. p. 210°, to a colourless liquid, decomp. 212°. It gives a reddish-yellow coloration with ferric chloride. The *hydrochloride* forms slender needles, m. p. 200—214°; the *aurichloride* forms golden-yellow, prismatic needles in tree-like aggregates, m. p. 172°; the *platinichloride* separates in stout, bright orange rods, decomp. 220°.

2-*Methylbenziminazole oxide*, $O<{N—C_6H_4 \atop CMe·NH}$, forms snow-white needles, m. p. 251°. The *hydrochloride* forms colourless needles; the *aurichloride* separates in golden-yellow, broad rods, m. p. 175° (decomp.); the *platinichloride*, in lustrous, yellow columns, m. p. 245°; the *sulphate* forms colourless needles or transparent plates, m. p. 174°. Those reagents which convert the lower homologue into phenylenecarbamide are without action. E. F. A.

Some Derivatives of Quindoline. FRITZ FICHTER and FRANZ ROHNER (*Ber.*, 1910, **43**, 3489—3499. Compare Fichter and Boehringer, Abstr., 1907, i, 92).—Quindoline is obtained in 75—80% yield by boiling the sodium salt of flavindine (quindolinecarboxylic acid) with 10% potassium hydroxide and zinc dust until the solution is colourless, filtering rapidly, and passing air through the filtrate, whereby quindoline is precipitated.

The reaction between quindoline and bromine in cold glacial acetic acid yields an unstable, dark yellow *bromo-perbromide*, $C_{15}H_{10}N_2Br_3$, which is converted by crystallisation from alcohol into 10-*bromoquindolinium bromide*, $C_{15}H_{10}N_2Br_2$, yellow needles; this substance, which contains

one ionisable bromine atom, is converted by alcoholic potassium hydroxide into 10-*bromoquindoline*, (annexed constitution), m. p. 304°, pale yellow needles. The position of the halogen atom is determined only by the fact that bromine first attacks the indole imino-group and then wanders to the para-position. The



attack of bromine at position 7 is rendered probable by the fact that substitution does not occur when 7-acetylquindoline and bromine react in glacial acetic acid; a dark red, unstable perbromide is obtained, which is converted by crystallisation into 7-*acetylquindolinium bromide*, $C_{17}H_{12}ON_2,HBr$, m. p. 272°, yellow needles, from which quindoline is produced by the action of alkalis.

A concentrated solution of quindoline in glacial acetic acid reacts with solid sodium nitrite, in the cold forming pale yellow needles of *quindolinium nitrite*, $C_{15}H_{10}N_2,HNO_2$, when heated yielding 7-*nitrosoquindoline*, m. p. 275°, dark red needles, which forms a blue solution in strong, alcoholic potassium hydroxide, and yields quindoline by hydrolysis with alcoholic hydrogen chloride. By reduction with tin and hydrochloric acid, quindoline is converted into 5 : 13-*dihydroquindoline*, m. p. 172° (rapidly heated), which is oxidised very easily, even by atmospheric oxygen, to quindoline. On treatment with acetic anhydride in the cold, dihydroquindoline yields 13-*acetyl*-5 : 13-*dihydroquindoline*, m. p. 162°, a monoacidic base, which oxidises less readily than dihydroquindoline. When boiled with acetic anhydride, dihydroquindoline is converted into 7 : 13-*diacetyl*-5 : 13-*dihydroquindoline*, m. p. 235°. Acetyldihydroquindoline and an excess of bromine in glacial acetic acid yield a yellow *perbromide*, from which 5 : 10-*dibromo*-13-*acetyl*-5 : 13-*dihydroquindoline*, m. p. 242°, is readily obtained. This substance suffers hydrolysis and oxidation when boiled with 40% sulphuric acid, yielding 5 : 10-*dibromoquindoline*, m. p. 221°, yellow needles.

13-*Methyl*-5 : 13-*dihydroquindolinium iodide*, $C_{16}H_{14}N_2HI$, is obtained by the methylation of dihydroquindoline or by the reduction of 13-methylquindolinium iodide by tin and hydrochloric acid, during which the *stannochloride*, $C_{16}H_{14}N_2,2HCl,SnCl_2$, is obtained. 13-*Methyl*-5 : 13-*dihydroquindolinium perchlorate*, $C_{16}H_{14}N_2,HClO_4$, obtained from an alcoholic solution of the iodide and perchloric acid, crystallises in golden leaflets. The base corresponding with these salts is so unstable that it changes in air into 13-methylquindolinium carbonate (*loc. cit.*).

C. S.

Pechmann's Isomeric Hydrazidines. MAX BUSCH and RICHARD RUPPENTHAL (*Ber.*, 1910, 43, 3001—3011).—Pechmann (Abstr., 1896, i, 32) has described two forms, m. p. 119° and 174° respectively, of diphenylbenzenylhydrazidine, to which he assigned the formulæ NHPh·CPh:N·NHPh and NPh:CPh·NH·NHPh, the isomerism being regarded as due to desmotropism.

It is now shown that the more fusible isomeride contains an asymmetric disubstituted hydrazine, and has the formula

NPh:CPh·NPh·NH_2.

It unites with aldehydes, forming hydrazones, and loses a nitrogen atom under the influence of nitrous acid, forming diphenylbenzenylamidine, NPh:CPh·NHPh.

The less fusible isomeride has the formula, NPh:CPh·NH·NHPh, assigned to it by Pechmann, and is converted on oxidation into the azo-compound, NPh:CPh·N:NPh.

By the interaction of benzanilide imide chloride and phenylhydrazine both isomerides are formed, the chloride attacking both the α- and β-nitrogen atoms of the hydrazine. The β-hydrazidine,

NPh:CPh·NH·NHPh,

predominates, and it was not found possible by altering the conditions to increase the proportion of the α-hydrazidine. The two isomerides are not convertible into one another. α-Diphenylbenzenylhydrazidine forms a stable *acetate*, soluble in very dilute acetic acid.

α-Diphenylbenzylidenebenzenylhydrazidine,

NPh:CPh·NPh·N:CHPh,

crystallises in colourless bunches of interlaced needles, which become yellow at 155°, m. p. 159—160°.

On leaving the α-diphenylbenzenylhydrazidine overnight with benzaldehyde in benzene solution, it decomposes, forming benzanilide.

Diphenyl-m-*nitrobenzylidenebenzenylhydrazidine* forms yellow needles, m. p. 173°.

The α-hydrazidine interacts with carbonyl chloride, forming a compound, $C_{20}H_{15}ON_3$, crystallising in microscopic, transparent prisms, m. p. 301—302°, which is considered to be end*oxytriphenyldihydrotriazole*, $NPh{<}{>}O\begin{array}{l}C{\equiv\equiv}N\\ \quad|\\ CPh{-}NPh\end{array}$.

Benzeneazophenyliminophenylmethane, NPh:CPh·N:NPh, crystallises in reddish-brown needles, m. p. 101—102°.

β-Diphenylbenzenylhydrazine, when boiled in alcoholic solution with benzaldehyde, forms *tetraphenyldihydrotriazole*, $NPh{<}\begin{array}{l}CHPh{\cdot}NPh\\ CPh{=}N\end{array}$, which separates in greenish-yellow needles, m. p. 119—120°.

Similarly, the β-hydrazidine unites with formaldehyde, yielding *triphenyldihydrotriazole*, $NPh{<}\begin{array}{l}CH_2{\cdot}NPh\\ CPh{:}N\end{array}$, which crystallises in stunted, transparent, greenish-yellow needles, softening at 120°, m. p. 124°, to a clear oil; it is faintly basic.

With carbonyl chloride, *triphenyltriazolone*, $NPh{<}\begin{array}{l}CO{-}NPh\\ CPh{:}N\end{array}$, is formed; it crystallises in colourless needles of silky lustre, m. p. 223—224°, and has neither basic nor acid properties. E. F. A.

Action of Phenylhydrazine on Ethyl Benzoylacetate. Otto Kühling (*Ber.*, 1910, **43**, 3399).—The product previously described (Abstr., 1910, i, 780) as ketoanilinodiphenyltetrahydrotriazine can be prepared by mixing acetic acid solutions of ethyl benzoylacetate and phenylhydrazine (excess). Whether the compound has the con-

stitution originally given or whether it is the phenylhydrazide of ethyl benzoylacetate phenylhydrazone has not been determined.

J. J. S.

Synthesis of Derivatives of 1 : 2 : 7-Pyrazopyridine [1 : 2 : 7-Benztriazole]: a New Series of Homo (C·C) Condensed, Heterodicyclic Compounds. CARL BÜLOW and KARL HAAS (*Ber.*, 1910, **43**, 3401—3412).—The fact that Walther's "5-imino-1-phenyl-3-methylpyrazolone" (Abstr., 1897, i, 297) contains a labile hydrogen atom attached to the carbon atom in the α-position to the carbon to which the amino-group is attached, and condenses with solutions of benzenediazonium salts (Michaelis, Abstr., 1905, i, 478), led the authors to the conclusion that the compound would condense with β-diketones or with esters of β-ketonic acids, yielding compounds of the types: $\begin{array}{l}\mathrm{CR{:}N{-}C{\cdot}NPh} \\ \mathrm{CH{:}CR'{\cdot}C{\cdot}CMe}\end{array}\!\!>\!\mathrm{N}$ and $\begin{array}{l}\mathrm{CR{:}N{-\!-}C{\cdot}NPh} \\ \mathrm{CH{\cdot}C(OH){\cdot}C{\cdot}CMe}\end{array}\!\!>\!\mathrm{N}$.

These are somewhat analogous to the hetero-condensed, heterocyclic condensation products already described (Abstr., 1909, i, 615; 1910, i, 80, 81, 203, 595), but contain a C·C-group common to the two nuclei in place of a C·N-group, and in addition the smaller ring contains a CH-group in place of a nitrogen atom. Monomethylene substituted β-ketones and β-ketonic esters react in a similar manner. The hydroxy-derivatives obtained when β-ketonic esters are used are not so strongly acetic as the heterohydroxylic acids previously described (Abstr., 1910, i, 595). As a rule, they cannot be titrated accurately by standard alkalis, using phenolphthalein as indicator, and solutions of their salts are decomposed by carbon dioxide. They form a link between the heterohydroxylic acids and the phenols proper.

1-*Phenyl*-3 : 4 : 6-*trimethyl*-1 : 2 : 7-*benztriazole*,

$$\begin{array}{l}\mathrm{CMe{:}N{-}C{\cdot}NPh} \\ \mathrm{CH{:}CMe{\cdot}C{\cdot}CMe}\end{array}\!\!>\!\mathrm{N},$$

obtained by boiling a glacial acetic acid solution of acetylacetone and 5-amino-1-phenyl-3-methylpyrazole for five hours, crystallises in large, colourless, compact, prismatic needles, m. p. 128°, and is feebly basic. The *aurichloride*, $C_{15}H_{15}N_3,HAuCl_4,H_2O$, forms long, glistening, yellow needles; the *platinichloride*, $2C_{15}H_{15}N_3,H_2PtCl_6,2H_2O$, crystallises in brown, compact, rhombic cubes, which change colour at 200°; the additive *compound* with silver nitrate forms long, colourless needles.

1-*Phenyl*-3 : 4 : 5 : 6-*tetramethyl*-1 : 2 : 7-*benztriazole*, $C_{16}H_{17}N_3$, prepared in a similar manner from methylacetylacetone, crystallises from alcohol in colourless needles, m. p. 138—139°, and 1 : 4-*diphenyl*-3 : 6-*dimethyl*-1 : 2 : 7-*benztriazole*, $C_{20}H_{17}N_3$, obtained from benzoylacetone, crystallises from 96% alcohol in slender needles, m. p. 136—137°, after sintering at 133°. It is sometimes accompanied by a by-product melting at 156—160°.

4-*Hydroxy*-1-*phenyl*-3 : 6-*dimethyl*-1 : 2 : 7-*benztriazole*, $C_{14}H_{13}ON_3$, obtained by boiling a glacial acetic acid solution of ethyl acetoacetate with the aminophenylmethylpyrazole, crystallises from hot water in glistening needles. It can be titrated by means of standard potassium

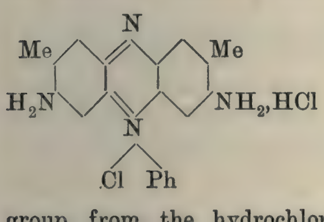
hydroxide solution, and the solution of the potassium salt gives precipitates with salts of most of the heavy metals. The *aurichloride*, $C_{14}H_{13}ON_3,HAuCl_4$, forms compact, yellow crystals, and the *platinichloride*, compact, yellowish-brown needles. The base has the properties of a feeble febrifuge. 4-*Hydroxy*-1-*phenyl*-3 : 5 : 6-*trimethyl*-1 : 2 : 7-*benztriazole*, $C_{15}H_{15}ON_3$, obtained from ethyl methylacetoacetate, crystallises from 90% alcohol in compact, rhombic plates, m. p. 224—226°; the *aurichloride* forms stout, yellow rods. 4-*Hydroxy*-1-*phenyl*-3 : 6-*dimethyl*-4-*ethyl*-1 : 2 : 7-*benztriazole*, $C_{16}H_{17}ON_3$, sinters at 181°, and has m. p. 183—184°.

The dissociation constant of 7-hydroxy-5-methyl-1:2:4:9-benztetrazole (Abstr., 1910, i, 595) is practically the same as that of valeric acid. J. J. S.

Synthesis of Safranines. III. N. N. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 939—949. Compare Abstr., 1910, i, 782—783).—The safranines can be readily obtained by the condensation of *p*-benzoquinonedichlorodi-imide or its homologues and analogues with 4-phenyltolylene-2 : 4-diamine or its homologues and analogues, the best yields being obtained with one molecule of the former to two of the latter. The safranines of various constitutions (containing benzene, toluene, or naphthalene nuclei) all have similar physical properties, their red colour becoming bluish as the molecular weight increases.

Aminoazotoluene, on reduction and subsequent treatment with bleaching powder, yields p-*toluquinonedichlorodi-imide*, $C_7H_6N_2Cl_2$, m. p. 74°, decomposes at 155°, and forms long, yellow, needle-shaped crystals.

3 : 7-*Diamino*-5-*phenyl*-2 : 8-*dimethylphenazonium chloride*, to which the annexed formula, namely, that of ordinary tolusafranine, is



assigned, obtained by the condensation of *p*-toluquinonedichlorodi-imide with 4-phenyltolylene-2 : 4-diamine, forms bright yellowish-green crystals. Alkali hydroxides precipitate the free *base* from ethereal solutions of the hydrochloride. The *dichromate*, $(C_{20}H_{19}N_4)_2Cr_2O_7$, was analysed. By removing one amino-group from the hydrochloride, 3-*amino*-5-*phenyl*-2 : 8-*dimethylphenazonium chloride* is formed. The aqueous solution is precipitated by picric acid, tannin, and sodium acetate. Ammonia and the alkali carbonates precipitate the *base*, of which the *dichromate*, $(C_{20}H_{18}N_3)_2Cr_2O_7$, was analysed.

The *acetyl* derivative of aminotolusafranine when treated with ammonia yields tolusafranine. When the second amino-group is removed from the monoamine, the chromogen, 5-*phenyl*-2 : 8-*dimethylphenazonium*, is obtained in the form of its ferric chloride compound,

$$C_{20}H_{17}N_2FeCl_4.$$

It forms brown crystals, m. p. 190°, which, when treated with ammonia and then with hydrochloric acid, yields dimethyl*apo*safranine hydrochloride, which is identical in all respects with the monoaminophenazonium from which the chromogen was obtained. Z. K.

Quinonoid Compounds. XXIV. Aniline-black. IV. RICHARD WILLSTÄTTER and CARL CRAMER (*Ber.*, 1910, **43**, 2976—2988. Compare Abstr., 1909, i, 535, 975).—Aniline-black is regarded as containing eight para-substituted benzene nuclei. The two stages of oxidation product contains three and four quinonoid nuclei respectively. A quantitative determination of these has been made by reduction with phenylhydrazine carbamate in an atmosphere of carbon dioxide and measurement of the nitrogen liberated. Reduction takes place in sharply differentiated stages, according to the temperature. In the case of dichromate black, one molecule of hydrogen is introduced at 30—35°, the colour changing to light blue; at 75—80° the colour becomes grey, and a further reduction takes place; lastly, between 120° and 150°, the colourless leuco-base is formed. The hydrolysed blacks are more stable; thus hydrolysed dichromate black is stable until 80°, loses a second quinonoid nucleus at 130—150°, and can only be completely reduced on the addition of a trace of Green's black, which acts as a catalyst. Chlorate-black contains four quinonoid nuclei; the first is attacked at 35—40°, the second at 80—110°, and the remaining two at 120—150°, the colour changing from dark violet through dull blue and brown to a light brownish-grey. Hydrolysed chlorate-black retains two nuclei at 150°, but parts with these in presence of Green's black.

Green's black, obtained on oxidising aniline salts with atmospheric oxygen in presence of copper sulphate and phenylenediamine, is very readily reduced, all four nuclei being attacked below 110°. When hydrolysed Green's black loses the quinonoid nuclei in turn at 80—100°, 115—130°, 130—140°, 140—150°. The behaviour of Green's black is attributed to the catalytic action of traces of impurity. The apparatus used is described and experimental data given of its testing with seven quinonoid compounds. E. F. A.

History of Diazohydrazides. EMIL FISCHER (*Ber.*, 1910, **43**, 3500—3501).—Dimroth and de Montmollin (Abstr., 1910, i, 898), in their account of the diazohydrazides, omit to mention that the first member of this class to be discovered was diazobenzene-ethylhydrazide, obtained by the author from diazobenzene chloride and ethylhydrazine in aqueous solution (*Annalen*, 1879, **199**, 306). C. S.

Biochemical Classification of the Proteins. JOSÉ RODRIGUEZ CARRACIDO (*Anal. Fis. Quim.*, 1910, **8**, 261—263; *Revista Chim.*, 1910, **6**, 314—315).—A scheme for the classification of the proteins founded more on biochemical than on chemical considerations.

W. A. D.

General Protein Chemistry. III. The Denaturation of Serum Albumin. LÉONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1910, **29**, 494—500).—If serum albumin is changed by heating, and then caused to coagulate by bringing the mixture to the isoelectric point, two stages in the denaturation can be detected. If the heating is not too long continued, the protein is obtained in the first stage of change, in which by the action of hydrochloric acid, it is rendered soluble and converted apparently in the original protein.

If the heating be continued for a longer time, the second stage is reached in which the coagulum is soluble in acid only with difficulty, and in which the reaction is irreversible. S. B. S.

The Fractional Precipitation of the Milk Proteins. ALBERT J. J. VANDERVELDE (*Biochem. Zeitsch.*, 1910, 29, 461—464).—As protein-α is described, that protein which is precipitated on the addition of acid, and as protein-β, that which separates from the filtrate from protein-α on coagulation. The author has estimated the amounts of these proteins in the whole milk, and in the fractions obtained by the additions of varying quantities of acetone, ethyl and methyl alcohols to the milk. From the results obtained, which are tabulated, the author draws the conclusion that it is not possible to conclude that milk caseinogen and milk albumin have distinct individuality. S. B. S.

Combination of Lactic Acid and Casein. W. VAN DAM (*Chem. Weekblad*, 1910, 7, 1013—1019).—By means of Bredig's ethyl diazoacetate method, the author has determined the reduction in the concentration of the hydrogen ions in solutions of lactic acid produced by addition of increasing amounts of casein. In solutions containing a large excess of hydrogen ions, the casein combines with a constant amount of lactic acid, 4·25%. Assuming that 1 molecule of lactic acid combines with 1 molecule of casein, the molecular weight of the protein is 2118. On the assumption that 1 molecule of potassium hydroxide neutralises 1 molecule of casein, Robertson (Abstr., 1910, ii, 679) gives 556 as the molecular weight. It follows that one basic group is present for every four replaceable hydrogen atoms in the casein molecule. A. J. W.

Electrochemistry of Proteins. III. Dissociation of Salts of Ovimucoid in Solutions of Varying Alkalinity and Acidity. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1910, 14, 709—718. Compare Abstr., 1910, ii, 679).—Mörner's ovimucoid, that part of the white of egg proteins which is not precipitated by boiling dilute acetic acid, but is precipitated by concentrated alcohol (Abstr., 1894, i, 264), was obtained as a dry white powder. It has been investigated by the method previously used with caseinogen.

Unlike caseinogen and globulin, ovimucoid dissolves readily, and is more basic than acidic. One gram requires $7·0 \times 10^{-5}$ gram-equivalents of hydrogen chloride to produce a solution which is neutral to litmus, and solutions containing less acid are alkaline. In very dilute potassium hydroxide solutions, ovimucoid tends to combine with the whole of the alkali, but the proportion of potassium hydroxide combined decreases with concentration, until in strongly alkaline solution the ovimucoid attains a maximum combining capacity of 50×10^{-5} gram-equivalents of alkali per gram.

The combining capacity for acid also increases, and tends to attain a constant value in presence of large excess of acid. The constant was never attained, but is probably greater than 100×10^{-5} gram-equivalents of acid per gram. The addition of ovimucoid to alkali or

acid of concentration less than $N/10,000$ increases the conductivity by reason of the considerable conductivity of the free protein. The conductivity of stronger solutions is considerably diminished by the protein. The depression in conductivity, λ, brought about by addition of 1% of ovimucoid to solutions of potassium hydroxide at 30° is expressed by $\lambda = 0{\cdot}2085b - 12{\cdot}5b^2 - 0{\cdot}000356$, and in the case of hydrogen chloride by $\lambda = 0{\cdot}4199a - 8{\cdot}527a^2 - 0{\cdot}000414$, where b and a are the concentrations of alkali and acid respectively. A similar expression was deduced in the case of caseinogen, in which, however, the factor c, the concentration of the protein, was introduced.

The author endeavours to trace a theoretical connexion between the constants 0·2085 and 0·4199 in the above equations, and the values 0·218 and 0·384 of the conductivities of potassium hydroxide and hydrogen chloride respectively at infinite dilution. R. J. C.

The Constitution of the Coloured Constituent of the Pigment of Blood. OSKAR PILOTY [with EUGEN QUITMANN and PAUL EPPINGER] (*Annalen*, 1910, **377**, 314—369. Compare Abstr., 1909, i, 539).—The acid previously termed hæmopyrrolecarboxylic acid is not derived from hæmopyrrole, but from an isomeride, and hence the name *phonopyrrolecarboxylic acid* is suggested; by the elimination of carbon dioxide from this acid, a dimethylethylpyrrole (*phonopyrrole*) is obtained, which is not identical with hæmopyrrole. Both compounds must be represented as dimethylethylpyrroles with a methyl group in position 2, and methyl and ethyl groups in positions 3 and 4 or 4 and 3. As phonopyrrolecarboxylic acid shows no tendency to yield an indole derivative, it is improbable that the methyl and $\cdot CH_2 \cdot CH_2 \cdot CO_2H$-groups are in the relative positions 2 and 3. This conclusion is confirmed by the fact that hæmatopyrrolidinic acid (Abstr., 1909, i, 540), which is formed by the union of molecular quantities of phonopyrrolecarboxylic acid and hæmopyrrole, on decomposition loses propionic acid from the phonopyrrolecarboxylic acid portion of the molecule, and yields 2 : 3-dimethylpyrrole. Phonopyrrole and its carboxylic acid must therefore have the two methyl groups in positions 2 and 3, and must be represented by the formulæ:

$$NH<\begin{matrix}CMe{:}CMe \\ CH{=}CEt\end{matrix} \quad \text{and} \quad NH<\begin{matrix}CMe{:}CMe \\ CH{=}C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H\end{matrix}$$

and hæmopyrrole as 2 : 4-dimethyl-3-ethylpyrrole, $NH<\begin{matrix}CMe{:}CEt \\ CH{=}CMe\end{matrix}$.

An ethereal solution of phonopyrrolecarboxylic acid reacts with a $0{\cdot}2N$-solution of benzenediazonium chloride, yielding a dark red *azo-dye*, $C_{15}H_{18}O_2N_3Cl$, m. p. 145—146° (decomp.). Phonopyrrolecarboxylic acid is scarcely affected when fused with potassium hydroxide at 300° for half an hour, or when distilled under very low pressures, but at atmospheric pressure it loses carbon dioxide at 250—330°, and gives a 28% yield of *phonopyrrole*, which is best purified by steam distillation. After distillation over barium oxide it has b. p. 96—98°/19 mm., and is readily distinguished from the isomeric hæmopyrrole, as it yields an oily *picrate*, which does not solidify when placed in a freezing mixture, and reacts with nitrous acid, yielding

a small amount of a syrupy maleinimide derivative (compare Abstr., 1910, i, 133).

Full details for the reduction of hæmatoporphyrin with tin and hydrochloric acid are given, and also for the preparation of hæmatopyrrolidinic acid free from tin. The acid is soluble in water to an appreciable extent, but yields precipitates with many salts and alkalis; these precipitates appear to be adsorption products. Hæmopyrrole forms an unstable compound with the acid. When the zinc derivative of the acid is fused with potassium hydroxide (compare Abstr., 1910, i, 857), water and the loosely-combined hæmopyrrole are evolved at 170—200°; at 270° a dark oil is formed, and the temperature is kept at 270° by dropping water gradually into the retort, but towards the end the temperature is raised to 320°.

The products isolated from the distillates are hæmopyrrole and 2 : 3-dimethylpyrrole, and from the residue, potassium acetate. The acetic acid must come from the portion of the hæmatopyrrolidinic acid which yields the 2 : 3-dimethylpyrrole, as the zinc compound of Kuster's hæmatic acid yields the acid $NH<\begin{matrix}CO\cdot CMe \\ \quad\,\, \| \\ CO\cdot C\cdot CH_2\cdot CH_2\cdot CO_2H\end{matrix}$ on oxidation, and this cannot be derived from hæmopyrrole. The formula suggested for hæmatopyrrolidinic acid is therefore

$$NH<\begin{matrix}CMe:CMe \\ \qquad\quad | \\ CH{=}C\cdot CH(CH_2\cdot CO_2H)\cdot\end{matrix}\begin{matrix}NH\cdot CMe \\ | \\ C{=}CMe\end{matrix}>CEt.$$

The constitution of the 2 : 3-dimethylpyrrole has been proved by the following method. The base yields methylmaleinimide, m. p. 105°, when oxidised by Willstätter and Asahina's method (Abstr., 1910, i, 499), and cannot therefore be an ethylpyrrole, 2 : 5-dimethyl- or 3 : 4-dimethyl-pyrrole, and, as it does not yield a crystalline azo-dye, cannot be 2 : 4-dimethylpyrrole (Marchlewski and Robel, Abstr., 1910, i, 206).

It is suggested that hæmin and hæmatin contain a group somewhat similar to that of hæmatopyrrolidinic acid (annexed formula).

On reduction, the 6-carbon ring can become ruptured at carbon atom No. 1 or 2. In the first case hæmatopyrrolidinic acid would be formed, and in the latter an isomeric acid. It is probable that the small yield of hæmatopyrrolidinic acid obtained when hæmatoporphyrin is fused with potassium hydroxide is due to the formation of this isomeric acid.

$$\begin{array}{l} \qquad\qquad\;\; {}^{2} \\ CMe{-\!-\!-}C\cdot C(CH_2\cdot CO_2H)\cdot C\cdot NH\cdot CMe \\ \|\qquad\quad \|\;\;\;| \qquad\qquad\qquad\; \| \qquad\quad \| \\ CMe\cdot NH\cdot C\cdot C(OH){-\!-\!-\!-\!-}C{-\!-\!-}CEt \\ \qquad\qquad\;\; {}_{1} \end{array}$$

The authors agree with Küster that the hæmins obtained from different sources have the same composition, and the product described by von Zeyneck (Abstr., 1900, i, 711) as having the composition $C_{34}H_{34}O_4N_5FeCl$ is shown to be impure hæmin, and, after purification by Schalféeff's method, has the composition of hæmin. The formula suggested is $C_{34}H_{33}O_4N_4FeCl$. The conversion of hæmin into hæmatin by means of alkali is usually regarded as due to the replacement of chlorine by hydroxyl. In further support of this view, it is now shown that hæmatin can be quantitatively transformed back into hæmin by adding a solution of the latter in chloroform containing quinine to a

hot glacial acetic acid solution of sodium chloride and stirring; after repeating the above operations, steel-blue, glistening crystals of pure hæmin are obtained (compare also Siewert, Abstr., 1908, i, 486), and as hæmin can be obtained from hæmatin prepared from hæmin or from oxyhæmoglobin, it follows that the products obtained from the two sources are identical.

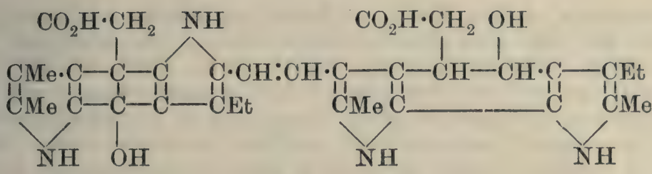
According to Nencki and Zaleski (Abstr., 1900, i, 709), hæmin contains two phenolic hydroxyl groups, as it can give dialkyl ethers which are insoluble in alkalis; these hydroxyl groups are also present in hæmatin, although, so far, hæmatin ethers have not been prepared. Hæmatin contains a third hydroxyl group, which is readily replaced by chlorine. This hydroxyl group is removed when the iron is withdrawn from the hæmatin molecule, and is, therefore, presumably attached to the iron atom. Hæmatin and hæmin do not appear to contain free carboxyl groups, but when the iron is removed from hæmin, the product, hæmatoporphyrin, is both distinctly acidic and basic, as it dissolves readily in both dilute acids and alkalis and forms well-defined salts. The development of basic properties is attributed to the removal of the iron which was previously attached to nitrogen, and the production of basic imino-groups. The iron in the hæmin molecule is thus in the tervalent condition, and when removed by the aid of hydrogen bromide, it is removed as ferric salt only, provided the temperature is not allowed to rise.

Küster's statement that a ferrous salt is formed is due to the fact that he used comparatively high temperatures, and the ferrous salt obtained was a secondary product formed by the reduction of the ferric salt. The authors used a modification of Nencki and Sieber's method for transforming hæmin into hæmatoporphyrin. Iron hæmatoporphyrin is regarded as the ferric salt of a carboxylic acid, and analyses agree fairly well with the formula $(C_{34}H_{35}O_5N_4)_3Fe$.

In the conversion of hæmin into hæmatoporphyrin, it is suggested that the carboxylic groups which were latent in hæmin become active. The presence of ethylene linkings in hæmatoporphyrin is proved by the readiness with which it is reduced by sodium amalgam, one molecule of the compound taking up 6 or 8 atoms of hydrogen; the solution of the leuco-base thus obtained reduces Fehling's solution and ammoniacal silver nitrate, and on the addition of acids yields a white precipitate of the leuco-base, which immediately turns brown on exposure to the air. The leuco-base cannot be obtained pure, but on oxidising the reduced solution by means of atmospheric oxygen and then acidifying, a product is formed which is apparently identical with deoxyhæmatoporphyrin. The production of this compound from hæmatoporphyrin probably takes place according to the equations: $C_{34}H_{38}O_6N_4 + 8H = C_{34}H_{44}O_5N_4 + H_2O$ and $C_{34}H_{44}O_5N_4 + 3O = C_{34}H_{38}O_5N_4 + 3H_2O$.

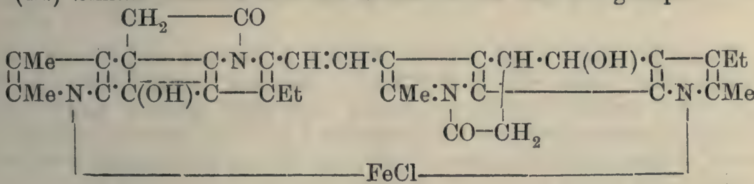
Schalféeff's method for the preparation of hæmin has been modified in several details, and a yield of 7·33 grams has been obtained from 1 litre of blood.

The following structural formulæ are suggested for hæmatoporphyrin (I), mesoporphyrin (II), and hæmin (III).



(I.)

(II.) Similar formula with 2H atoms for the two OH groups.



(III.)

Attention is drawn to the fact that these formulæ cannot be regarded as established beyond question, as they are based to a large extent on the reactions of hæmatopyrrolidinic acid, a compound which it is impossible to obtain in a pure state. J. J. S.

Hæmin Dimethyl Ether. William Küster (*Ber.*, 1910, 43, 2960—2962).—Hæmin dimethyl ether (Nencki and Zaleski, Abstr., 1900, i, 710) is easily prepared in quantity by adding hæmin dissolved in chloroform containing a little pyridine to a boiling mixture of methyl alcohol and strong hydrochloric acid. It is a black powder consisting of aggregates of microscopic needles, and dissolves in pyridine, probably with the formation of a dimethyl ether of hæmin-pyridinium chloride. On the addition of water, a colloidal solution is formed, from which the dye is precipitated by a few drops of nitric acid, chlorine remaining in the solution. E. F. A.

The Decomposition of Blood-pigment. F. Bardachzi. **Compounds of Pyridine in Blood-pigment.** Ernst Kalmus. **Pyridine Compound of Hæmochromogen.** Richard von Zeynek (*Zeitsch. physiol. Chem.*, 1910, 70, 205—216, 217—223, 224—229).—On heating oxyhæmoglobin with 10% alkali, the fluid first shows the spectrum of alkali-hæmatin, and on prolonged heating, of hæmochromogen. Proofs are adduced that this is really hæmochromogen, and not an alkali compound of that substance. In carbon monoxide hæmochromogen, the gas is less firmly combined than it is in carboxyhæmoglobin ; it can be removed in a vacuum at room temperature by boiling, or by a stream of pure hydrogen. An apparatus is also described for obtaining the gases evolved on the heat coagulation of blood-pigment.

The two last papers agree in regarding the crystals obtained by the action of pyridine on blood-pigment as a pyridine compound of hæmochromogen, and not as Kobert and Dilling state, as hæmochromogen itself. Dilling's statement that hæmochromogen does not give the guaiacum reaction is also said to be incorrect. W. D. H.

Valency of the Metal in Blood-pigments, and the Estimation of the Gas Combining Power. A Critical Study. WILHELM MANCHOT (*Zeitsch. physiol. Chem.*, 1910, 70, 230—249).—Kuster states that hæmoglobin and hæmochromogen are ferrous compounds, and bases his conclusion partly on Hüfner's investigations on the uptake of nitric oxide by solutions of metallic salts. The bulk of the present paper is occupied in showing that Hüfner's method is not trustworthy, that hæmoglobin is a ferric compound, and that in hæmocyanin the copper is probably present in the cupric state.

W. D. H.

Yeast Nucleic Acid. III. PHŒBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1910, 43, 3150—3163. Compare Abstr., 1909, i, 620, 686).—On hydrolysing yeast nucleic acid with mineral acids, the following components have been obtained: adenine, guanine, cytosine, uracil, *d*-ribose, and phosphoric acid, but it was not certain whether cytosine and uracil are primary decomposition products or formed by the decomposition of the purine bases.

It is now shown that cytosine is not derived from the purine bases, and that it is not fixed in the nucleic acid molecule as a pentoside. On partial hydrolysis of nucleic acid with ammonia, *cytidine*,

$$C_9H_{13}O_5N_3,$$

is obtained; it forms crystalline derivatives; thus the *picrate* has m. p. 185—187°, the *sulphate*, m. p. 233°, the *hydrochloride*, m. p. 218°. The free base has $[\alpha]_D^{20}$ $+19{\cdot}14°$, the *sulphate* having $[\alpha]_D^{30}$ $+29{\cdot}7°$.

Cytidine is hydrolysed to cytosine only by concentrated acids or by heating under pressure; neither pentose nor lævulic acid is formed, yet cytidine gives a faint orcinol reaction.

A crystalline acetyl derivative could not be obtained. The *tribenzoyl* derivative crystallises in long, prismatic needles, m. p. 205°; it could not be acetylated.

Nitrous acid effects the quantitative elimination of the amino-group from cytidine, and *uridine* is obtained, crystallising in long, prismatic needles, m. p. 165°, $[\alpha]_D^{30}$ $+5{\cdot}15°$.

The relation of amino-acid nitrogen to the total nitrogen in nucleic acid is 3 : 15; this figure confirms the presence of uracil in the molecule, since uracil does not contain an amino-group, whilst the other three bases each contain one, so that were uracil absent the relation should be 3 : 13.

By the action of nitrous acid, adenosine is converted into inosine identical with that obtained from carnine. Similarly, guanosine gave xanthosine.

E. F. A.

Triticonucleic Acid. PHŒBUS A. LEVENE and FREDERICK B. LA FORGE (*Ber.*, 1910, 43, 3164—3167).—It is probable that yeast nucleic acid and the triticonucleic acid discovered in wheat embryos by Osborne and Harris (compare also Osborne and Heyl, Abstr., 1908, i, 376) are identical. Triticonucleic acid on partial hydrolysis gives the nucleosides guanosine and adenosine, and also cytidine, that is, the same complexes as were obtained by Levene and Jacobs (Abstr., 1909, i, 620, 686) from yeast nucleic acid.

E. F. A.

The Pentose from the Pancreas. PHŒBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1910, **43**, 3147—3150).—Polemical. The authors (Abstr., 1909, i, 447, 620) have shown that the pentose in inosic acid, guanylic acid, and yeast nucleic acid is *d*-ribose, the optical antipode of the *l*-ribose synthesised by Alberda van Eckenstein and Blanksma. Rewald (Abstr., 1909, i, 858) identifies the pentose as xylose. Nucleoprotein prepared from the pancreas by Salkowski's method is now shown to give ribose and no trace of xylose (compare Neuberg, Abstr., 1909, i, 686). E. F. A.

The Pentose from the Pancreas. CARL NEUBERG (*Ber.*, 1910, **43**, 3501—3502).—In reply to Levene and Jacobs' criticism (preceding abstract) of his work (Abstr., 1909, i, 686), the author points out that their process does not determine whether different nucleic acids and pentoses occur in the pancreas, and also calls attention to the many contradictory statements of Levene concerning the pancreas nucleic acid. C. S.

The Pentose from the Pancreas. BRUNO REWALD (*Ber.*, 1910, **43**, 3502—3503).—Levene's identification of the pentose from the nucleic acid of the pancreas, guanylic acid, and similar nucleic acids as *d*-ribose depends on the rotation of a very dilute solution of its osazone (Levene and Jacobs, above). In the author's experiments (Abstr., 1909, i, 858) more than a gram of material was used. C. S.

Prolylglycineanhydride Formed by the Tryptic Digestion of Gelatin. PHŒBUS A. LEVENE (*Ber.*, 1910, **43**, 3168—3170).—Prolylglycineanhydride, $[\alpha]_D$ $-55°$, was obtained by the tryptic digestion of gelatin extending over eight months (Levene and Beatty, Abstr., 1906, i, 718), whereas the same peptide obtained synthetically by Fischer and Reif (Abstr., 1908, i, 1007) had $[\alpha]_D$ $-217°$. A product obtained after twenty-four days' tryptic digestion had $[\alpha]_D$ $-169°$, and the conclusion is drawn that the peptide becomes racemised during the prolonged action of the enzyme. E. F. A.

The Sulphur and Cystine in the Keratin of Birds. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1910, **69**, 310—312).—Keratin from goose feathers contains 3·15% sulphur and 6·3% cystine; from hen's claws, 2·28% sulphur and 2·14% cystine; from the epidermic scales of hen's toes, 2·2% sulphur and 1·88% cystine. Hofmann and Pregl (Abstr., 1907, i, 884) state that the horny material from the bird's stomach, which they term koilin, contains no cystine; in the present research it was found to contain rather more than 0·5%.
W. D. H.

Iodoproteins. HENRY L. WHEELER and LAFAYETTE B. MENDEL (*Biochem. Zeitsch.*, 1910, **29**, 417—419). CARL NEUBERG (*ibid.* 420—421).—Polemical (compare Abstr., 1910, i, 704, ii, 143). S. B. S.

The Dissociation Constants of Tryptophan. ARISTIDES KANITZ (*Biochem. Zeitsch.*, 1910, **29**, 126—129).—These have been

calculated from the data given for specific rotation of the amphoteric substance, and for the hydrochloride and sodium salts in acid and alkaline solutions. From these, $K_b = 1 \cdot 1 \times 10^{-13}$, and $K_s = 1 \cdot 3 \times 10^{-11}$.
S. B. S.

The Inactivation of Ferments and the Production of Anti-Ferments in vitro in the Presence of Artificial Membranes. A. E. PORTER (*Quart. J. exp. Physiol.*, 1910, **3**, 375—390. Compare Abstr., 1910, i, 601).—Certain enzymes can be inactivated by contact with artificial membranes, especially those made of collodion. At the same time the solution acquires inhibitive properties. Possibly in the body, the living membranes act in the same way. Only traces of the enzyme can be recovered from the membrane, the inactivating power of which increases with use. The inhibitive power is only in part due to substances previously in the solution, and the question arises whether the anti-enzyme which appears combines with the enzyme or acts on the substrate as Cramer and Bearn suggest for their zymoids; the latter explanation is adopted as the main one.
W. D. H.

Influence that the Reaction [of the Medium] Exerts on Certain Properties of Malt Macerations. AUGUSTE FERNBACH and M. SCHŒN (*Compt. rend.*, 1910, **151**, 894—897. Compare Abstr., 1906, i, 327; Maquenne and Roux, *ibid.*, i, 327).—The resistance of malt diastases to the action of heat is closely connected with the reaction of the medium in which they are present. If this is rendered neutral to methyl-orange, the amylolytic power of the malt is increased, but the resistance to heat is diminished. On the other hand, the stability is greater in a medium neutral to phenolphthalein, but hydrolytic activity is diminished. Auto-activation is at a maximum when the malt macerations are neutral to phenolphthalein.
W. O. W.

Influence of Different Temperatures on Ferments and on the Regeneration of Fermentative Properties. M. J. GRAMENITZKI (*Zeitsch. physiol. Chem.*, 1910, **69**, 286—300).—Taka diastase in aqueous solutions loses its fermentative properties at 80°, but recovers at temperatures below 45°, slowly at the ordinary temperature, and more quickly at 40°. Similar results were obtained after heating to 115°, the ferment not being destroyed, but only losing temporarily its fermentative power.

The oxydase maltin retains its oxidising power to a slight extent after being heated for ten minutes at 100°. Longer heating (fifteen to twenty minutes) results in complete loss of power for a time; the oxydase recovers its properties, however, after a certain time. When subjected to higher temperatures, the oxydase loses its properties beyond recovery.

At 80° the oxydase not only loses (temporarily) its oxidising properties, but acquires the power of deoxidising.

Solutions of maltin, after being heated for ten minutes at 100°, retain the power of dissolving starch, but no longer produce sugar.
N. H. J. M.

Influence of Temperature on the Activity of Cellase. GABRIEL BERTRAND and ARTHUR COMPTON (*Compt. rend.*, 1910, **151**, 1076—1079. Compare Abstr., 1910, i, 212, 290).—The optimum temperature for the hydrolysis of cellose by cellase prepared from sweet almonds is about 46°. The fatal temperature, at which the enzyme is rapidly destroyed, is about 75—76°, but the preparation loses its activity more slowly at lower temperatures. W. O. W

Hydrolysis of Amygdalin by Emulsin. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1910, **248**, 534—535).—The hydrolysis of amygdalin by emulsin occurs in three stages, each of which is caused by a particular enzyme. The amygdalin, under the influence of amygdalase, first yields α-dextrose and mandelonitrileglucoside (Auld, Trans., 1908, **93**, 1276); the latter is then decomposed by a β-glucosidase into β-dextrose and *d*-benzaldehydecyanohydrin, which is split by δ-*d*-oxynitrilase into benzaldehyde and hydrogen cyanide.

The new facts on which these statements are based are the following. A 5% solution of emulsin, after being heated for ten hours at 60—65°, hydrolyses *d*-benzaldehydecyanohydrin, but not amygdalin; conversely, the filtrate obtained after saturating a solution of emulsin with magnesium sulphate, hydrolyses amygdalin, but not *d*-benzaldehydecyanohydrin.

The primary formation of *d*-benzaldehydecyanohydrin in the hydrolysis of amygdalin is proved by the fact that the filtrate mentioned above, which cannot contain oxynitrilase or the synthetic enzyme, produces a considerable amount of *d*-benzaldehydecyanohydrin by its action on amygdalin. The view that *d*-benzaldehydecyanohydrin is also produced in a secondary reaction (Abstr., 1910, i, 403) is supported by the fact that *d*-benzaldehydecyanohydrin is produced by the action of emulsin on prulaurasin, a glucoside of the corresponding *i*-nitrile.

C. S.

Synthetical Enzyme Action. II. JACOBUS H. VAN'T HOFF (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, **48**, 963—970. Compare Abstr., 1909, ii, 988).—The behaviour of glucosides of tertiary alcohols towards emulsin in presence of their solid products of hydrolysis, and moistened with solutions saturated with these products, has been studied by means of volume changes. Hydrolysis, on account of the taking up of water, is accompanied by contraction; synthesis of the glucoside causes expansion. A small dilatometer was employed. In the case of the hydrolysis of the natural glucosides salicin, arbutin, and æsculin by emulsin, contraction was observed of a magnitude corresponding with the complete hydrolysis of the glucoside. With tertiary alcohol glucosides, emulsin has no synthetic action. This is analogous to the behaviour of the tertiary alcohols on etherification.

Primary alcohols are readily etherified. No glucoside of a solid primary alcohol was available for investigation, but a mixture of dextrose hydrate, glycerol, and emulsin, set aside at 31°, showed a diminution in the amount of dextrose from 0·305 to 0·211 dextrose per gram of the mixture after twenty-five days, and the quantity increased on diluting with an emulsin solution or heating with dilute hydrochloric acid for an hour. With anhydrous dextrose instead of

the hydrate, no condensation was observed. The best results were obtained with a mixture of 2 parts of dextrose hydrate, 4 parts of glycerol, 1 part of water. When used in molecular proportions, about 70% of glycerol and dextrose are converted into glucoside. The rate of synthetic action was proportional to the quantity of enzyme. Of two different enzyme preparations, the most active synthetically was also that most active in promoting hydrolysis. E. F. A.

Isomerisation of Some Phosphorus Compounds. II. ALEXANDER E. ARBUSOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 549—561. Compare Abstr., 1910, i, 802).—The thiophosphinites of the type $PR_2\cdot SR'$ under the catalytic influence of alkyl iodides undergo similar processes of isomerisation into the sulphides PSR_2R' to the corresponding oxygen compounds, but in the former the reaction is complicated by the formation of by-products.

Ethyl diphenylthiophosphinite, $PPh_2\cdot SEt$, obtained by the action of sodium mercaptide on diphenylphosphoryl chloride, has b. p. 196·5—197°/13 mm., D_0^0 1·1330, and gives double salts with the copper halides, of which the *copper iodide* compound is described. When treated with ethyl iodide in a sealed tube at 100°, it yields *diphenylethylphosphine sulphide*, $PSEtPh_2$, which crystallises in colourless, rhombic tablets, m. p. 65·5—66° ; diphenyldiethylphosphonium iodide, PPh_2Et_2I, m. p. 207—208°, the platinichloride of which has m. p. 202—203° (Michaelis, *Annalen*, 1881, **207**, 215, gives m. p. 218°) ; *ethyl diphenyloxythiophosphinate*, $PPh_2O\cdot SEt$, m. p. 72—73° ; diphenylphosphinic acid, crystallising in bright prisms, m. p. 194—195°, and probably *ethyl diphenylthiophosphinate*, $PPh_2S\cdot SEt$. iso*Butyl diphenylthiophosphinite*, $PPh_2\cdot S\cdot C_4H_9$, was prepared by the action of sodium *iso*butylmercaptide on diphenylphosphoryl chloride. It is a colourless liquid, b. p. 200·5—201°/8 mm., D_0^0 1·0892, and forms a crystalline *additive* compound with copper iodide. Under the catalytic influence of *iso*butyl iodide at 115°, it is converted almost quantitatively into *diphenyl*iso*butylphosphine sulphide*, $PSPh_2\cdot C_4H_9$, forming rhombic crystals, m. p. 80—81°, but if the mixture be subjected to prolonged gentle heating at 80°, *diphenyldi*iso*butylphosphonium iodide*,

$$PPh_2(C_4H_9)_2I,$$

m. p. 183—184°, is obtained. Sodium *iso*amylmercaptide when treated with diphenylphosphoryl chloride forms iso*amyl diphenylthiophosphinite*, $PPh_2\cdot S\cdot C_5H_{11}$, b. p. 219—220°/12 mm., D_0^{17} 1·0645, which, with *iso*amyl iodide at 120°, yields chiefly *diphenyl*iso*amylphosphine sulphide*, $PSPh_2\cdot C_5H_{11}$, large, bright, rhomboid crystals, m. p. 63·5°.

Sodium propylmercaptide with diphenylphosphoryl chloride yields only a small quantity of *propyl diphenylthiophosphinite*, $PPh_2\cdot SPr$, b. p. 229—230°/28 mm., which with propyl iodide is rapidly isomerised at 99° into *diphenylpropylphosphine sulphide*, $PSPh_2Pr$, crystallising in thin tablets, m. p. 97—98°. Z. K.

Organic Chemistry.

Formation of Hydrocarbons from Carbon Monoxide. LÉO VIGNON (*Bull. Soc. chim.*, 1911, [iv], 9, 18—20).—Various observers have shown that when carbon monoxide is passed over heated sodium or potassium hydroxide, soda-lime, or calcium hydroxide, a formate is produced, and that on further heating hydrogen is evolved. In the present investigation it is shown that with lime and carbon monoxide between 350° and 400° considerable quantities of methane, ethylene, and hydrogen are formed, and that from 400° to 600° the quantity of hydrogen increases at the cost of the hydrocarbons. The reactions taking place are probably represented by the following equations:

$$2CO + Ca(OH)_2 = (H\cdot CO\cdot O)_2Ca = C_2O_2(O)_2Ca + H_2;$$
$$2(H\cdot CO\cdot O)_2Ca + CaO = 3CaCO_3 + CH_4;$$
$$4(H\cdot CO\cdot O)_2Ca + 2CaO = 6CaCO_3 + C_2H_4 + 2H_2,$$

and experiments in heating calcium formate or oxalate alone and mixed with lime have confirmed this explanation of the origin of the hydrocarbons. Carbon monoxide may be converted into hydrogen and hydrocarbons to the extent of 99·5% by passage over hot lime several times, and it is suggested that in this way illuminating gas might be freed from this toxic constituent. T. A. H.

A Secondary Heptane in Roumanian Petroleum. N. COSTĂCHESCU (*Ann. sci. Univ. Jassy*, 1910, 6, 294—301).—The fraction of petroleum from Colibasi having b. p. 87·5—93·5° contains β-methylhexane with 1 : 3-dimethyl*cyclo*pentane and a small quantity of isomeric heptanes. When the fraction is heated with nitric acid (D 1·4) at 60° in sealed tubes, the β-methylhexane is converted mainly into a *nitro*-derivative, $C_7H_{15}O_2N$, b. p. 86—86·5°/21·5 mm., D_0^0 0·9961, n_D 1·43855; the other hydrocarbons, however, undergo oxidation to oxalic acid and carbon dioxide. W. O. W.

Dimorphism of Iodoform. BRUNO BARDACH (*Chem. Zeit.*, 1911, 35, 11—12).—The thin, yellow needles obtained previously (Abstr., 1909, i, 645) by the action of iodine and potassium iodide on acetone solutions of anhydrides and anhydride-forming compounds are now found to consist of iodoform. The crystals have m. p. 121°, and, on distilling in steam or crystallising from alcohol, are transformed into the ordinary hexagonal form. F. B.

Estimation of Active Hydrogen in Organic Compounds by means of Magnesium Methyl Iodide. TH. ZEREWITINOFF *Ber.*, 1910, 43, 3590—3595. Compare Abstr., 1907, ii, 509; 1908, i, 593).—The method previously described for the determination of replaceable hydrogen atoms is applicable also to the alkaloids. Those alkaloids which contain active hydrogen react with magnesium methyl iodide at the ordinary temperature, and yield methane quantitatively.

When heated, no additional methane is formed, showing the alkaloids to contain no amino-group. The rapidity of the method and the fact that only small quantities of substance are required are important features. A number of the commoner alkaloids were tested.

Pseudo-acids from nitromethane, nitroethane, etc., react as if they contained one hydroxyl, although the amount of methane obtained is somewhat less than the calculated, but it increases on warming. The experiments were made both in amyl ether and in pyridine solution; xylene, mesitylene, and anisole may equally well be used.

E. F. A.

[Pinacolin Derivatives] Corrections. Maurice Delacre (*Bull. Soc. chim.*, 1911, [iv], 9, 41—43).—Polemical in reply to Richard (this vol., i, 6), claiming priority as regards the synthesis of the alcohol $CMe_3 \cdot CHMe \cdot OH$ (Abstr., 1906, i, 477) and other matters.

T. A. H.

Preparation of Octan-$\gamma\eta$-dione-α-ol and its Homologues. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 227177).—The condensation of unsaturated ketones, by which 1:5-diketones are obtained, is a reaction about which very little is known; the diketo-alcohols now described are of technical importance in pharmacological preparations.

Octan-$\gamma\eta$-dione-α-ol, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot OH$, b. p. 142—143°/22 mm., a colourless, odourless oil, miscible with water in all proportions, is prepared as follows: methyleneacetone (Abstr., 1910, i, 652) is mixed with water (15 parts), either alone or in the presence of a small quantity of potassium carbonate, and allowed to remain until the odour of methyleneacetone has disappeared; the solution is acidified with tartaric acid, saturated with ammonium sulphate, and the product extracted with ether, dried, and fractionated, when a considerable amount of butan-γ-on-α-ol, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot OH$, b. p. 84—85°/23 mm., is also obtained.

$\beta\zeta$-Dimethyloctan-$\gamma\eta$-dione-α-ol is prepared by boiling methyl methylene-ethyl ketone with aqueous formic acid during forty to fifty hours, unchanged methyl methylene-ethyl ketone is removed by steam, and the solution rendered alkaline, whereby any *formyldimethyloctandionol* is hydrolysed. The product, a viscous, odourless, colourless oil, b. p. 145·5°/16 mm., 148°/18 mm., and 264—268° under atmospheric pressure, can also be obtained by either boiling dimethyloctendione (this vol., i, 114) with water, or by shaking it with cold dilute formic or with sulphuric acid; the *semicarbazone* has m. p. 209—210°.

F. M. G. M.

Preparation of Narcotics [Glyceryl Ethers]. C. F. Boehringer and Söhne (D.R.-P. 226454).—Glyceryl triethyl ether is not a narcotic, but when mixed alkyl residues are introduced, this property is developed; these compounds are colourless, mobile fluids.

Glyceryl $\alpha\gamma$-dimethyl β-ethyl ether, $C_7H_{16}O_3$, b. p. 65°/20 mm., D^{20} 0·917, was prepared by the ethylation of the $\alpha\gamma$-dimethyl ether in benzene solution with the necessary quantity of sodium ethoxide and

ethyl bromide. *Glyceryl αγ-dimethyl β-propyl ether*, $C_8H_{18}O_3$, was similarly obtained with propyl chloride; it has b. p. 76—77°/17 mm., and D^{20} 0·908. *Glyceryl β-methyl αγ-diethyl ether*, $C_8H_{18}O_3$, has b. p. 75°/17 mm., D^{20} 0·902.

Glyceryl αβ-dimethyl γ-ethyl ether, $C_7H_{16}O_3$, b. p. 49°/7—8 mm., D^{20} 0·919, was prepared from glycerol ethyl ether, methyl iodide, and sodium methoxide in benzene solution.

Glyceryl αγ-diethyl β-propyl ether, $C_{10}H_{22}O_3$, has b. p. 77—78°/9—10 mm., and D^{20} 0·882.

Glyceryl αβ-dimethyl γ-propyl ether, $C_8H_{18}O_3$, b. p. 66—67°/9—10 mm., D^{20} 0·910, was obtained from *glycerol propyl ether*, b. p. 122°/12 mm., D^{22} 1·024, which was prepared by the action of sodium propoxide on glycerol monochlorohydrin.

Glyceryl α-methyl βγ-diethyl ether, $C_8H_{18}O_3$, b. p. 57°/7—8 mm., D^{20} 0·901, was prepared from *glycerol methyl ether*, b. p. 108—109°/8—10 mm., D^{20} 1·115. *Glyceryl β-benzyl αγ-dimethyl ether*, $C_{12}H_{18}O_3$, has b. p. 149—150°/17—18 mm., and D^{20} 1·023. *Glycerol α-ethyl γ-propyl ether*, b. p. 86·5°/10 mm., D^{20} 0·935, was prepared from the sodium derivative of glycerol ethyl ether and propyl bromide, and yielded on methylation *glyceryl β-methyl α-ethyl γ-propyl ether*, $C_9H_{20}O_3$, b. p. 71·5—72°/7—8 mm., D^{20} 0·893. F. M. G. M.

A Very Basic Chromic Acetate. ERNST GUSSMANN (*Zeitsch. anorg. Chem.*, 1911, **69**, 217—220).—In the preparation of hexa-acetatotripyridinetrichromi-diacetate (Abstr., 1910, i, 503) it was found that the mother liquors contained a violet basic acetate, $Cr_2(OAc)_3(OH)_3,9H_2O$. This is best obtained as follows: To a solution of 10 grams of hexa-acetatotrichromium diacetate (Abstr., 1909, i, 757) in 15 grams of water are added 10 grams of pyridine, and the solution heated for half a day. After separating the crystals of the above-mentioned diacetate of the tripyridine base, the mother liquor is allowed to evaporate at room temperature. After several weeks the crystals are collected, and washed with cold water to remove the admixed diacetate of the tripyridine base. Rapid concentration of the solution is not favourable to the formation of crystals.

The violet acetate forms violet, four-sided double pyramids, and loses $9H_2O$ over sulphuric acid. It readily dissolves in dilute acids, giving a violet solution, which makes it probable that the hydroxyl groups possess an hydroxo- and not an ol-character. In phenol it gives a normal molecular weight. It is also formed when a solution of the diacetate of the trichromium base is repeatedly evaporated, or when a solution of freshly cold-precipitated chromium hydroxide in acetic acid is allowed to evaporate at room temperature.

A green, amorphous basic acetate has also been obtained by drying the diacetate of the hexa-acetatotrichromium base at 100—110°. It is less basic than the violet acetate. A formula cannot be given for it at present. T. S. P.

Behaviour of Acetic Anhydride at a High Temperature. EUGEN BAMBERGER (*Ber.*, 1910, **43**, 3517—3520).—According to the author, the first stage in the formation of acetone, by the distillation

of calcium acetate, is the dissociation of the salt into calcium oxide and acetic anhydride, which at the high temperature necessary for its production decomposes into carbon dioxide and acetone. With a view to confirming this supposition, the behaviour of acetic anhydride at high temperatures has been studied. On heating the anhydride for several hours at 290—300°, small quantities of acetone and acetylacetone were found amongst the products. Whether the formation of the last-named substance is due to the direct acetylation of acetone by means of acetic anhydride, or to the intermediate formation of keten, has not been determined.

These experiments also support the contention of Schmidlin and Bergmann (Abstr., 1910, i, 816) that the first stage in the synthesis of keten from acetic anhydride (Wilsmore, Trans., 1907, **91**, 1938) consists in the decomposition of the latter into carbon dioxide and acetone.

The reaction $O(COMe)_2 = CO_2 + COMe_2$ is probably reversible, but the amounts of carbon dioxide and acetone are very small, when equilibrium is attained.

The fact that acetone is produced in large quantity by the distillation of calcium acetate is not in opposition to this view, for the dissociation products, carbon dioxide and acetone, are continuously removed during the reaction, the latter by distillation, the former by union with the calcium oxide, produced by the decomposition of the acetate.

Various by-products obtained in the manufacture of acetone were examined for acetylacetone, but no indication of its presence was obtained. F. B.

Salts of a Green and of a Violet Propionatochromium Base. RUDOLF F. WEINLAND and KARL HOEHN [with M. FIEDERER] (*Zeitsch. anorg. Chem.*, 1910, **69**, 158—178. Compare Abstr., 1908, i, 847).—Salts of the *green hexapropionatotrichromium* base, $Y(OH)_3$, where $Y = \left[Cr_3{}^{(O\cdot COEt)_6}_{(OH_2)_2}\right]$. To prepare the *dichromate propionate*, $Y(O\cdot COEt)(Cr_2O_7),H_2O$, 2 grams of chromium trioxide are warmed with 20 c.c. of propionic acid. After filtering from the undissolved chromium trioxide, the solution, on keeping, deposits four-sided, brownish-green plates of the salt in question. Molecular weight determinations in acetophenone gave 961—801, as against 937·6. The *sesquichromate propionate*, $Y(O\cdot COEt)(HCrO_4)(\frac{1}{2}CrO_4)$, is obtained by warming chromium trioxide and chromium hydroxide, in the proportion of 2 mols. of the former to 1 mol. of the latter, with propionic acid. On concentrating the solution, dark olive crystals are obtained. Molecular weight in acetophenone was 753—878, as against 877·5. When a mixture of chromium trioxide and chromium hydroxide in the molecular proportion of 1 : 3 is dissolved in propionic acid and the solution concentrated, green, six-sided plates of the *chromate propionate*, $Y(O\cdot COEt)(CrO_4),1\cdot5H_2O$, are obtained. It may also be obtained by dissolving 1 gram of chromium trioxide in 50 c.c. of propionic acid and concentrating the solution.

When less than ten parts of propionic acid to one part of chromium

trioxide are taken and the mixture heated, chromates are obtained which contain less propionic acid in the anion than the above-mentioned salts. Whether a dichromate or a lower chromate of the base is obtained depends on the time of heating; the longer the heating, the poorer is the resulting chromate in chromic acid.

Whenever the dichromate propionate is recrystallised from a little water, propionic acid is lost from the anion, and pure *sesquichromate*, $Y(CrO_4)(\frac{1}{2}CrO_4),2H_2O$, is obtained. Even when the chromate propionates are recrystallised from a solution of propionic acid, some of the latter is split off from the anion.

The *chloride chromate*, $Y(CrO_4)Cl,H_2O$, is obtained as yellowish-green, six-sided plates by the addition of concentrated hydrochloric acid to strong solutions of any of the above salts. The *monopropionate*, $Y(O{\cdot}COEt),2H_2O$, is prepared from the chromate propionates by removing the chromic acid with lead propionate, or from the chloride (Abstr., 1908, i, 935) by treatment with silver propionate; it forms pale green, rod-like crystals.

Salts of a *violet pentapropionatotrichromium* base, $Y(OH)_2$, where $Y = \left[\begin{matrix}(O{\cdot}COEt)_5 \\ Cr_3(OH)_2 \\ (OH_2)_2\end{matrix}\right]$. The *dipropionate*, $Y(O{\cdot}COEt)_2$, forms the starting point for the preparation of the other salts. It is best prepared by dissolving 1 mol. of freshly-prepared chromium hydroxide, which has been washed with cold water, in 3 mols. of propionic acid at the room temperature. The solution is then heated in a sealed tube for five hours at 140—160°; on cooling, violet crystals of the dipropionate are found on the walls of the tube. After purification by a somewhat complicated method they are obtained as flat prisms, which may be 1 cm. long. Molecular weight in acetophenone was 615, as against 737·7. The *monopropionate*, $Y'(O{\cdot}COEt),3H_2O$, where $Y' = \left[\begin{matrix}(CEtO_2)_5 \\ Cr_3(OH)_3 \\ H_2O\end{matrix}\right]$, is obtained by saturating the aqueous solution of the dipropionate with sodium chloride or nitrate; light violet crystals. The *sesquipropionate*, $Y(O{\cdot}COEt)_2,Y'O{\cdot}COEt,H_2O$, results on evaporating a solution of one part of the dipropionate with five parts of sodium propionate; violet, flat prisms. The *sulphate propionate*, $(YO{\cdot}COEt)_2SO_4,4H_2O$, crystallises in violet plates on the addition of concentrated sulphuric acid to the saturated solution of the dipropionate. The *bromide propionate*, $Y(O{\cdot}COEt)Br,4H_2O$, forms violet prisms, as also does the *chloride*, $Y'Cl,Y'O{\cdot}COEt,10H_2O$; they are formed from the dipropionate by precipitation with concentrated hydrobromic and hydrochloric acid respectively.

All the salts of the violet base are readily soluble in ether and chloroform; those of the green base are insoluble in ether. The salts of the violet base cannot be recrystallised from water.

From the solution of chromium chloride hydrate, $CrCl_3,6H_2O$, in a solution of sodium propionate, violet crystals are obtained having the composition $Cr(O{\cdot}COEt)_2{\cdot}OH,H_2O$. They are insoluble in ether, in contradistinction to the violet pentapropionatotrichromium salts.

T. S. P.

Condensation of αβ-Dibromopropaldehyde with Malonic Acid. ROBERT LESPIEAU (*Compt. rend.*, 1910, 151, 1359—1361. Compare Spenzer, Abstr., 1905, i, 204).—αβ-Dibromopropaldehyde acts on malonic acid to form *βγδ-tribromovaleric acid*, m. p. 128—130°; the *ethyl* ester has b. p. 160—161°/12—13 mm. Both the acid and the ester, on treatment with zinc and alcohol, furnish *ethyl* Δ^{β}-*pentenoate*, $CHMe{:}CH{\cdot}CH_2{\cdot}CO_2Et$, b. p. 145—146°/760 mm. On brominating the corresponding acid, a substance is obtained probably identical with αβ-dibromovaleric acid. W. O. W.

The Oil and Wax of Coffee Beans. HANS MEYER and ALFRED ECKERT (*Monatsh.*, 1910, 31, 1227—1251).—Unroasted coffee beans, from which the greater part of the caffeine had been extracted, were dried, powdered, and digested with benzene. The oil thus obtained had a brownish-yellow colour, was nearly odourless, and had the consistency of olive oil. On hydrolysis it gave 21·2% of non-saponifiable matter. For isolating the acids formed on hydrolysis, it was found advisable to saponify with lithium hydroxide solution (compare Partheil and Ferié, Abstr., 1904, i, 4), but this method did not give a complete separation of saturated from unsaturated acids. The sparingly soluble lithium salts gave the following acids: Carnaubic acid, 10% (Stürcke, Abstr., 1884, 1280; Darmstädter and Liefschütz, 1896, i, 346; Dunham and Jacobson, 1910, i, 215); daturic acid, 1—1·5% (Gerard, Abstr., 1890, 1396; Kreis and Hafner, 1903, i, 788; Holde, Ubbelohde, and Marcusson, 1905, i, 318); palmitic acid, 25—28%, and decoic acid, 0·5%.

In order to obtain the carnaubic acid pure, the least soluble fraction of the lithium salts was transformed into chloride by means of thionyl chloride and then into ester; the processes of conversion into lithium salt, chloride, and ester were repeated, when the *methyl* ester was obtained in the form of glistening plates, m. p. 54—55°, and this on hydrolysis gave the acid with m. p. 74° (not 70° or 72·5°). The *lead* salt has m. p. 109—110°, and is soluble in toluene. The acid resembles stearic acid in many respects, but its ethyl ester is not so soluble in alcohol. The detection of glyceryl esters of this acid in fats is readily accomplished by warming the fat with absolute alcohol and a little sulphuric acid, when the sparingly soluble ethyl carnaubate mixed with a little palmitate and stearate is deposited.

Methyl daturate, $C_{16}H_{33}{\cdot}CO_2Me$, has m. p. 30°, and the *magnesium* salt, m. p. 137—142°.

The more soluble lithium salts were converted into lead salts, and the saturated and unsaturated acids separated by extraction with benzene. The acids isolated were palmitic, oleic 2%, and linoleic 50%. The unsaturated acids were identified by oxidation with 2% permanganate solution in the cold, when dihydroxystearic and sativic acids were obtained, and by bromination, when tetrabromostearic acid was isolated.

The wax contained a small amount of alkaloid, which was removed by steam distillation and solution in glacial acetic acid. When finely divided and made into an emulsion with potassium hydroxide solution, the wax was oxidised by 4% permanganate to carnaubic acid, and when

hydrolysed with alcoholic potassium hydroxide solution at 150—170°, it gave carnaubic acid (50%) and a compound with the properties of a tannol. This latter has not been obtained crystalline; it has no definite m. p., but is soluble in alkali solutions and can be benzoylated. The wax is therefore a tannol resin. J. J. S.

Preparation of Compounds of Unsaturated Acids with Aldehydes, Ketones, and Formic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 226222 and 226223).—It is found that unsaturated fatty acids of high molecular weight combine (in the presence of acid condensing agents) with ketones or aldehydes to form a new series of oily compounds. The free acid may be replaced by the oil, which under the experimental conditions becomes almost entirely hydrolysed. The substances employed were acetone, formaldehyde, acetaldehyde, benzaldehyde, dextrose, lævulose, sucrose, and maltose, which were severally heated with castor oil, ricinoleic acid, oleic acid, and cottonseed oil in the presence of either sulphuric acid, zinc chloride, or phosphoryl chloride. The second patent states that formic acid may be employed in this reaction instead of formaldehyde, and details are given of its condensation with ricinoleic acid.

F. M. G. M.

Preparation of Acyl Derivatives of Castor Oil [Ricinoleic Acid]. VEREINIGTE CHININFABRIKEN ZIMMER & CO. (D.R.-P. 226111. Compare Abstr., 1909, i, 696).—The aromatic acyl derivatives of ricinoleic acid have not previously been prepared; it is now found that aromatic acid chlorides reacting with the hydroxyl group of the acid yield the corresponding acyl derivative; these are usually tasteless, odourless oils.

The *benzoyl* ester was prepared by boiling castor oil in benzene solution with benzoyl chloride in the presence of pyridine during half an hour; the *anisoyl* ester was obtained in a similar manner. The *salicyl* ester was prepared by heating castor oil and salol together at a temperature of 200° during three hours, and distilling off the separated phenol in a vacuum. F. M. G. M.

Ester Condensations with Chloroacetic Ester. WILHELM WISLICENUS (*Ber.*, 1910, 43, 2528—2533).—In the Claisen condensation, ethyl chloroacetate can function as the ester component and also as the methylene compound.

The interaction of ethyl chloroacetate, ethyl oxalate, and sodium ethoxide in ethereal solution yields ethyl chloro-oxalacetate,

$$CO_2Et \cdot CO \cdot CHCl \cdot CO_2Et,$$

b. p. 150—152°/56 mm. (compare Peratoner, Abstr., 1893, i, 11; Roubleff, Abstr., 1891, 223); this forms a green *copper* salt, and yields oxamide when treated with ammonia; at 240° it loses only half the theoretical amount of carbon monoxide; in alcoholic solution it gives an intense red ferric chloride reaction.

When equal molecular quantities of ethyl formate and ethyl chloroacetate are introduced into a cold alcoholic ethereal solution of potassium methoxide, a *potassium* salt is formed, from which, by

acidification, *ethyl α chloroformylacetate*, $CHO\cdot CHCl\cdot CO_2Et$, is obtained as an oil giving an intense violet ferric chloride reaction. On repeated distillation in a vacuum, it is obtained in colourless leaflets, m. p. 88—90°; the latter give only a faint violet coloration with ferric chloride, and yield with copper acetate a green *copper* salt; after fusion, the crystalline ester gives the original, intense violet ferric chloride reaction. The isomerism here exhibited has not been further investigated, but there is little doubt that the liquid ester has the enolic structure, $OH\cdot CH:CCl\cdot CO_2Et$.

The *benzoyl* derivative, $OBz\cdot CH:CCl\cdot CO_2Et$, prepared from the above-mentioned potassium salt, crystallises from alcohol in large, colourless plates, m. p. 90—91°. With phenylhydrazine, both the ester and the potassium salt react to form the osazone of ethyl β-hydroxypyruvate, $CH(:N\cdot NHPh)\cdot C(:N\cdot NHPh)\cdot CO_2Et$ (compare Will, Abstr., 1892, 356).

The condensation of two molecules of ethyl chloroacetate has also been effected (compare Erlenbach, Abstr., 1892, 953); ethyl chloroacetate (2 mols.) and sodium ethoxide (1 mol.), free from alcohol, are allowed to react in ethereal solution at a low temperature; on acidifying the *sodium* salt thus produced, *ethyl α-γ-dichloroacetoacetate*, $CH_2Cl\cdot CO\cdot CHCl\cdot CO_2Et$, is obtained in an impure condition. It is purified by converting it into the copper salt and decomposing this with hydrochloric acid; it forms a colourless oil with a penetrating odour, b. p. 118—120°/15 mm., and solidifies on cooling, m. p. 18—20°; it gives an intense cherry-red coloration with ferric chloride, and is hydrolysed by boiling with dilute sulphuric acid to *s*-dichloroacetone; the *copper* salt, $(CH_2Cl\cdot CO\cdot CCl\cdot CO_2Et)_2Cu$, crystallises in microscopic, green needles, melting at 149° (decomp.) to a turbid yellow liquid. F. B.

Ethyl γ-Chloroacetoacetate. ROBERT LESPIEAU (*Bull. Soc. chim.*, 1911, [iv], 9, 31—33. Compare Abstr., 1899, i, 243; 1905, i, 406; Picha, Abstr., 1907, i, 178).—Polemical with Schlotterbeck (Abstr., 1909, i, 550) on the physical properties of this ester.

T. A. H.

Condensation of Ethyl Acetate with its Higher Homologues. ANDRÉ WAHL (*Compt. rend.*, 1911, **152**, 95—98).—It has hitherto been found impossible to prepare β-ketonic esters by condensing ethyl acetate with its higher homologues. This condensation has now been effected by adding alternately to the higher ester, small, carefully weighed portions of ethyl acetate and sodium. In this way the formation of ethyl acetoacetate and of the compound

$$R\cdot CO\cdot CHR\cdot OH$$

is prevented or diminished; the yield, however, is small, 5—6% in the case of ethyl propionylacetate for the pure compound, and 18—20% in the case of ethyl butyrylacetate. The latter forms a green *copper* derivative, $Cu(C_8H_{13}O_3)_2$, m. p. 125—126°; on boiling with methyl alcohol it changes into a blue *basic* salt, $C_8H_{13}O_3\cdot CuOMe$.

Ethyl butyrylacetate is converted by oxides of nitrogen into *ethyl butyrylglyoxylate*, $CH_2Et\cdot CO\cdot CO\cdot CO_2Et$, an orange-yellow liquid, b. p.

87—88°/13 mm., becoming colourless on the addition of water or alcohol, with which it combines; the diketone condenses with *p*-phenylenediamine, forming *ethyl* 2-*propylquinoxaline*-3-*carboxylate*,

$$C_6H_4\!<\!\begin{matrix}N:CPr^{\alpha}\\ \vert\\ N:C\cdot CO_2Et\end{matrix}$$

long needles, m. p. 63—64°. W. O. W.

γ-Ethoxy-α-alkylacetoacetic Esters. MARCEL SOMMELET (*Bull. Soc. chim.*, 1911, [iv], 9, 33—38. Compare Abstr., 1907, i, 21, 107).—The considerable differences in the boiling points ascribed by Isbert to the compounds he regarded as α-ethoxybutanone and α-ethoxypentanone (Abstr., 1886, 1009) from those found by the author for his preparations of these substances has led him to re-investigate esters having the constitution assigned by Isbert to the esters from which his ketones were prepared. The author finds that they do not correspond with Isbert's descriptions, and that on hydrolysis they furnish ketones identical with those he has described already (*loc. cit.*).

Ethyl γ-*ethoxy*-α-*methylacetoacetate*, $OEt\cdot CH_2\cdot CO\cdot CHMe\cdot CO_2Et$, D_4^0 1·033, D_4^{17} 1·017, b. p. 112—114°/14 mm., 116·5—118·5°/19 mm., obtained by condensing ethoxyacetonitrile with ethyl α-bromopropionate in presence of zinc (compare Blaise, Abstr., 1901, i, 252), is a faintly yellow liquid, which reduces ammoniacal silver nitrate in the cold, and gives a violet coloration with ferric chloride. On hydrolysis with potassium hydroxide solution, the ester yields α-ethoxybutanone, and with hydrazine hydrate gives a *pyrazolone*, m. p. 135—137°, which crystallises from boiling water.

Ethyl γ-*ethoxy*-α-*ethylacetoacetate*, $D_4^{14\cdot5}$ 1·0157, b. p. 125—128°/18 mm., similarly obtained, resembles its lower homologue, and on hydrolysis gives α-ethoxypentanone, and with hydrazine hydrate furnishes a *pyrazolone*, m. p. 99—99·5°, which crystallises from boiling water in hard prisms.

Ethyl γ-*ethoxy*-αα-*dimethylacetoacetate*, D_4^0 1·065, D_4^{17} 1·047, b. p. 114—116°/17 mm., 111—113°/14 mm., obtained by condensing ethyl bromo*iso*butyrate with ethoxyacetonitrile in presence of zinc, is a pale yellow liquid, reduces ammoniacal silver nitrate, and on alkaline hydrolysis furnishes *ethoxymethyl* iso*propyl ketone*, $OEt\cdot CH_2\cdot COPr^{\beta}$, b. p. 160° (approx.), which gives a *semicarbazone*, m. p. 128—129·5°. Along with the ester there is formed in this condensation a small quantity of a *substance*, $C_{12}H_{19}O_4N$, m. p. 90—91·5°, which crystallises in needles or prisms, is soluble in strong acids, becomes yellow in contact with alkali, and gives no coloration with ferric chloride. Heated with alkali in a closed tube, it evolves ammonia and furnishes a trace of *iso*butyric acid and an unidentified oily product.

T. A. H.

Iso- and Hetero-poly-acids. II. Oxalato-tellurates. ARTHUR ROSENHEIM and M. WEINHEBER (*Zeitsch. anorg. Chem.*, 1911, 69, 261—265. Compare this vol., ii, 116).—Concentration of a solution containing molecular proportions of telluric acid and an alkali oxalate leads to the deposition of crystals of the oxalato-tellurates. The potassium, rubidium, and cæsium salts have the general formula

$M_2C_2O_4,H_6TeO_6$, where M = K, Rb, or Cs, and crystallise in stellar aggregates of needles. The effect of heat on these salts shows that the water is firmly combined, so that telluric acid hydrate, H_6TeO_6, and not the anhydride, TeO_3, is probably contained in the complex anion. These compounds should therefore be formulated as

$$M_2[H_6TeO_6C_2O_4].$$

Their solubilities increase from the potassium, through the rubidium, to the cæsium salt, this being the opposite order to what generally obtains with salts of these metals. Comparison of the solubility of the potassium salt with the solubilities of potassium tellurate and oxalic acid shows that a great diminution in solubility has taken place, pointing to complex formation. This could not be verified by conductivity measurements, however, owing to the hydrolysis which takes place.

Homogeneous ammonium or sodium oxalato-tellurates could not be obtained. T. S. P.

Molecular Rearrangements in the Camphor Series. VI. *iso*Campholactone. William A. Noyes and A. W. Homberger (*J. Amer. Chem. Soc.*, 1910, 32, 1665—1669).—In an earlier paper (Abstr., 1909, i, 133) the authors described a compound obtained by the action of nitric acid on *iso*campholactone, which they regarded as a dilactone of the composition $C_8H_{13}O_4$. It has now been found that this substance is, in reality, a nitrolactone.

*iso*Campholactone, prepared by Noyes and Taveau's method (Abstr., 1904, i, 807), gave $[\alpha]_D^{28}$ $-63·1°$ in an 8·8% solution in alcohol; Noyes and Taveau found $[\alpha]_D$ $-60·7°$ in a 5% solution.

On heating *iso*campholactone with ammonium hydroxide in a sealed tube at 100°, it yields the *ammonium* salt of the corresponding acid, m. p. 137°, which is re-converted into the lactone when left in the air. When the lactone is heated with nitric acid (D 1·27), a mixture of products is obtained, the chief of which is *nitro*iso*campholactone*, $NO_2·C_8H_{13}<\begin{matrix}CO\\|\\O\end{matrix}$, m. p. 122°, b. p. 272°, which crystallises in needles, and has $[\alpha]_D$ $-85·4°$ in a 5·5% solution in alcohol. A monobasic lactonic *acid*, $C_9H_{12}O_4$, m. p. 138°, was isolated from the mother liquor, which has $[\alpha]_D$ $-42·05°$ in a 6% solution in alcohol; its *barium* salt was prepared; the *amide* has m. p. 164°.

*Amino*iso*campholactone*, $NH_2·C_8H_{13}<\begin{matrix}CO\\|\\O\end{matrix}$, m. p. 84°, obtained by reducing nitro*iso*campholactone with tin and hydrochloric acid, forms small crystals, and is decomposed by sodium hydroxide with formation of a compound, m. p. 152°. *Hydroxylamino*iso*campholactone*,

$$OH·NH·C_8H_{13}<\begin{matrix}CO\\|\\O\end{matrix},$$

m. p. 144°, prepared by treating nitro*iso*campholactone with zinc dust and acetic acid, forms small, stellate crystals, is slightly basic, and readily reduces Fehling's solution.

When nitro*iso*campholactone is shaken with 0·5*N*-sodium hydroxide until completely dissolved, and afterwards acidified with hydrochloric

acid, an *acid*, $C_5H_8O_2N\cdot CO_2H$, m. p. 73—74°, is produced ; its *barium* salt crystallises in needles containing $2\frac{1}{2}H_2O$. By the action of ammonium hydroxide on nitro*iso*campholactone, the corresponding *amide*, m. p. 96—97°, is obtained. E. G.

Molecular Rearrangements in the Camphor Series. VII. Derivatives of *iso*Camphoric Acid; *l*-Hydroxydihydrocampholytic Acid. WILLIAM A. NOYES and LUTHER KNIGHT (*J. Amer. Chem. Soc.*, 1910, **32**, 1669—1674).—*d*- and *l*-*iso*Camphoric acids are usually regarded as *cis*- and *trans*-isomerides. As, however, the evidence of this structure does not seem altogether conclusive in the case of the latter compound, the present work was undertaken in order to throw some light on the question. Assuming that *iso*camphoric acid is stereoisomeric with camphoric acid, α is used in this paper to denote the secondary carboxyl, and β the tertiary carboxyl, group.

By boiling *iso*camphoric acid with methyl alcohol and sulphuric acid, the α-methyl and dimethyl esters are obtained. The *dimethyl* ester, $C_8H_{14}(CO_2Me)_2$, b. p. 146°/27 mm., has D^{20} 1·073, D^{25} 1·069, and $[\alpha]_D^{21}$ $-65·2°$; a 10% solution in alcohol has $[\alpha]_D$ $-63·6°$. The *α-methyl* ester, m. p. 88°, crystallises in needles, and gives $[\alpha]_D$ $-57·9°$ in a 10% alcoholic solution ; its *amide*, m. p. 157°, crystallises in plates, and has $[\alpha]_D$ $-60·05°$ in a 10% alcoholic solution.

β-iso*Camphoramic acid*, $CO_2H\cdot C_8H_{14}\cdot CO\cdot NH_2$, m. p. 165—166°, obtained by hydrolysing the α-methyl ester amide with sodium hydroxide, crystallises in needles. When its sodium salt is treated with sodium hypobromite solution, *amino*iso*dihydrocampholytic acid*, $CO_2H\cdot C_8H_{14}\cdot NH_2$, m. p. 225—227°, is produced ; its *hydrochloride* and *lead* salt are described. When this acid is heated at 250—300°, it is converted into an *anhydride*, which furnishes a *nitroso*-compound, m. p. 194°. If amino*iso*dihydrocampholytic acid hydrochloride is treated with a solution of sodium nitrite, there are produced a hydrocarbon, a lactone, *d*-campholytic acid, and l-*hydroxydihydrocampholytic acid*, $CO_2H\cdot C_8H_{14}\cdot OH$, m. p. 132°, which forms granular crystals and gives $[\alpha]_D$ $-70·04°$ in an aqueous solution containing 1·45%. The formation of this compound, instead of hydroxydihydro*iso*campholytic acid, which was expected, renders it probable that the former is the more stable, and that part of the hydroxydihydro*iso*campholytic acid is converted into it by the action of the nitrous acid, or else that *d*-campholytic acid is formed as an intermediate product and unites with water to produce *l*-hydroxydihydrocampholytic acid. E. G.

Saccharinic Acids. HEINRICH KILIANI (*Ber.*, 1911, **44**, 109—113).—A reply to Nef (Abstr., 1910, i, 714). The phenylhydrazide of α-metasaccharin has m. p. 145°, as previously found, and not 113—115°, as stated by Nef.

The trihydroxyadipic acid described by Kiliani and Eisenlohr (Abstr., 1909, i, 553) is not identical with the old trihydroxy-acid ; it has m. p. 159—160°, whereas a mixture of the two melts at 142—145°. The silver salt also does not crystallise in the small plates characteristic of the silver salt of the old acid. The presence of

a compound with a branched chain in parasaccharin has been confirmed by reduction to α-ethylbutyrolactone, and the isolation of this in the form of Chanlaroff's calcium salt, $3Ca(C_6H_{11}O_3)_2,2H_2O$ (Abstr., 1885, 374). The yield of calcium salt, however, is small, and large quantities of syrupy salts are formed.

By oxidising parasaccharin with nitric acid to parasaccharone (Abstr., 1904, i, 975) and reducing this with hydriodic acid, a small amount of *n*-adipic acid has been obtained. These results indicate that parasaccharin must be a mixture.

Nef's parasaccharin (α-*d*-galactometasaccharin) does not appear to be hygroscopic, whereas the author's preparations are excessively hygroscopic.

The acid obtained by the oxidation of barium parasaccharinic acid is not hydroxycitric acid, as stated previously (Abstr., 1904, i, 976), but *l*-tartaric acid. J. J. S.

Glucodeconic Acids. L. H. PHILIPPE (*Compt. rend.*, 1910, **151**, 1366—1367. Compare this vol., i, 12).—On evaporating an aqueous solution of β-glucodeconic acid, a mixture of two compounds is obtained: (1) the hydrated β-*lactone*, $C_{10}H_{18}O_{10},H_2O$, crystallising in hemihedral needles, m. p. 135° (anhydrous, m. p. 193°), $[\alpha]_D^{17} - 41{\cdot}2°$; (2) an *anhydride*, $C_{20}H_{38}O_{21}$, separating in microscopic granules resembling those of starch, m. p. 216—218°, $[\alpha]_D$ about $-10°$. The lactone is the chief constituent in dilute solutions, whilst the anhydride predominates in concentrated solutions. The β-lactone is also formed when the α-lactone is heated at 140° in pyridine.

Sodium β-glucodeconate is gummy, but the *barium*, *cadmium*, and *strychnine* salts are crystalline. The *β-phenylhydrazide* crystallises in needles, m. p. 246°, and is ten times more soluble in water than the α-compound. W. O. W.

Derivatives of Aldol and Crotonaldehyde. RUDOLF WEGSCHEIDER and ERNST SPÄTH (*Monatsh.*, 1910, **31**, 997—1029).—The authors have examined the behaviour of aldol towards acetylating agents under various conditions, and find that acetylation is accompanied by the formation of condensation products; loss of water and rupture of the aldol molecule also occur.

When aldol is boiled with acetic anhydride in the presence of a little sulphuric acid, ethylidene acetate and *aldol triacetate*,

$$OAc{\cdot}CHMe{\cdot}CH_2{\cdot}CH(OAc)_2,$$

are produced. The latter substance is a colourless oil, b. p. 138—140°/12 mm., which yields crotonaldehyde when boiled with water or alkalis; when treated with bromine in chloroform solution, it is converted into bromocrotonaldehyde.

Gentle acetylation of aldol with acetic anhydride and sulphuric acid in benzene or chloroform solution yields, amongst other products, *aldol monoacetate*, $OAc{\cdot}CHMe{\cdot}CH_2{\cdot}CHO$; it is a colourless oil, b. p. 87—89°/18 mm., and is also obtained by the action of acetic acid and a little sulphuric acid on aldol at the ordinary temperature.

By heating aldol with acetic anhydride alone, Wurtz (this Journ., 1872, 808) obtained two substances, which he considered to be croton-

aldehyde diacetate and acetylaldol. The authors have repeated Wurtz's experiments, and find that his crotonaldehyde diacetate consists of a mixture of aldol triacetate and a compound $C_{12}H_{18}O_5$, whilst the substance described as acetylaldol is identical with crotonaldehyde diacetate. The *compound*, $C_{12}H_{18}O_5$, is probably the diacetyl derivative of dialdan, $C_8H_{14}O_3$, a substance obtained by Wurtz by the action of acids on aldol; it is produced by gently acetylating aldol with acetic anhydride and sulphuric acid, either alone or in chloroform and benzene solution, and also by the action of acetic and sulphuric acids on aldol at the ordinary temperature; the b. p. varies from 144—147°/13 mm. to 152—154°/12 mm., according to the method of preparation, but whether this variation is due to impurity or the presence of two dialdan diacetates has not been decided. The constitution of the compound is discussed, and arguments advanced in favour of the formula OAc·CHMe·CH(CHO)·CH(OAc)·CH:CHMe.

The following condensation products were also isolated and examined: a *diacetate* of $C_{12}H_{20}O_2$, colourless oil, b. p. 201—203°/10 mm., produced by acetylating aldol with acetic anhydride in the presence of a little sulphuric acid, and probably having the structure

$$\begin{matrix}\text{CHMe·O·CHMe} \\ | \\ \text{CH}_2\text{—CH(OAc)}\end{matrix}\!\!>\!\text{C}\!<\!\!\begin{matrix}\text{CHO} \\ \text{CH(OAc)·CH:CHMe}\end{matrix}$$

; a *substance*, $C_{18}H_{30}O_7$, b. p. 228—233°/13 mm., obtained by the action of a mixture of acetic and sulphuric acids on aldol, and represented as a monoacetyl derivative of

$$\begin{matrix}\text{OH·CHMe·CH(CHO)·CH(OH)} \\ \text{CHMe:CH·CH(OH)}\end{matrix}\!\!>\!\text{C}\!<\!\!\begin{matrix}\text{CHMe———O} \\ \text{CH(OH)·CH}_2\text{·CHMe}\end{matrix};$$

a mixture of the monoacetyl derivatives of $C_8H_{14}O_3$ and $C_8H_{16}O_4$, produced by acetylating aldol with acetic anhydride and sulphuric acid in chloroform solution.

Acetyl chloride reacts with aldol in benzene solution, forming α-chlorocrotyl acetate, CHMe:CH·CHCl·OAc, b. p. 76—77°/18 mm.; the same substance is also produced by the addition of acetyl chloride to crotonaldehyde. When aldol is acetylated by means of acetic anhydride in the presence of sodium acetate, the main product is crotonaldehyde diacetate.

Aldolphenylhydrazone is obtained in an impure condition by the action of phenylhydrazine on aldol in ethereal solution; it is a viscid oil, b. p. 196°/10 mm.; the p-*nitrophenylhydrazone* crystallises in reddish-yellow needles, m. p. 109—111°, with previous sintering at 107°; *aldoloxime* has b. p. 117—118°/11 mm.

Crotonaldehydephenylhydrazone, prepared by the action of phenylhydrazine on crotonaldehyde in alcoholic solution at 35—42°, is a yellow oil, b. p. 156—158°/11 mm. (compare Trener, Abstr., 1901, i, 232); the p-*nitrophenylhydrazone* crystallises in brown needles, m. p. 184—185°.

The authors also describe two new condensation products of acetaldehyde. A specimen of crotonaldehyde, which had been kept for three and a-half months in a closed glass vessel filled with carbon dioxide, yielded on distillation an *oil*, $C_{10}H_{18}O_4$, b. p. 88—95°/16 mm., and a viscid *liquid*, $C_{16}H_{28}O_6$, b. p. 156—161°/16 mm. It is suggested

that these two substances are produced by the condensation of acetaldehyde, derived from the para-aldehyde (with which the original crotonaldehyde was probably contaminated) according to the equations: $C_{10}H_{18}O_4 = 5C_2H_4O - H_2O$ and $C_{16}H_{28}O_6 = 8C_2H_4O - 2H_2O$. F. B.

Preparation of Octendione and its Homologues. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 227176).—The methylene ketones employed in the following reactions were recently described (Abstr., 1910, i, 652); it is now found that they polymerise readily, yielding octendiones (and higher polymerides) of considerable therapeutic importance.

Δ_a-*Octen-γη-dione*, b. p. 75—76°/21 mm., a colourless oil, sparingly soluble in water, and with a penetrating odour, is prepared by the long boiling of methyleneacetone under reflux, and subsequent fractional distillation of the products: its *semicarbazone* has m. p. 199°.

βζ-Dimethyl-Δ^a-octen-γη-dione, COMe·CHMe·CH_2·CH_2·CO·CMe:CH_2, is prepared in a similar manner from methyl methylene-ethyl ketone, but owing to the higher temperature employed more of the higher polymerides are simultaneously produced; it is a colourless, highly refractive oil, b. p. 187—194° or 83—85°/17 mm., with pine-like odour, immiscible with water, and slowly decomposed by boiling at atmospheric pressure into its progenitors; its *semicarbazone* has m. p. 183°. Dimethyloctendicne can also be obtained by the slow distillation in a vacuum of βζ-dimethyloctan-γη-dione-α-ol (see this vol., i, 102) with an equal weight of hydrogen potassium sulphate, or by boiling it with acetic anhydride.
F. M. G. M.

The Influence of Inactive Substances on the Rotation of Lævulose. NEUMANN WENDER (*Biochem. Zeitsch.*, 1911, **30**, 357—373).—The addition of inorganic acids to a solution of lævulose was found in most cases to increase the specific rotation, the increase varying with the degree of acidity of the solution. Inorganic salts as well as organic acids varied in their behaviour, causing in some cases a rise, in others a decrease, in the rotation. Alcohols and acetone produced a marked diminution in the rotation, which was proportional to the amount added. W. J. Y.

Mercerised Cellulose. CHARLES F. CROSS (*Ber.*, 1911, **44**, 153—154).—In connexion with Miller's results (this vol., i, 17) it is pointed out that bleached cotton is not a homogeneous cellulose, and that by the action of sodium hydroxide solution the β-celluloses are dissolved. Previous heating at 90—100° renders the β-celluloses still more reactive towards alkalis. The increase in weight of the cellulose on hydration is compensated by the loss in weight due to the removal of the β-celluloses (compare Cross and Bevan, "Cellulose," pp. 4 and 28).

The author upholds the view that a definite series of hydrated celluloses exists, and that these are stable within the limits 0° to 50°.
J. J. S.

Mercerised Cellulose. CARL G. SCHWALBE (*Ber.*, 1911, **44**, 151—152. Compare preceding abstract).—Attention is drawn to the

fact that during treatment with sodium hydroxide solution a portion of the cellulose is dissolved.

Previous experiments (Abstr., 1908, ii, 627) have shown that mercerised cellulose does not contain water (compare also Ost and Westhoff, Abstr., 1909, i, 210).

According to Liebermann (*Dingler's polyt. J.*, 1886, **181**, 133) an aqueous solution of rosaniline base does not dye cotton-cellulose. For behaviour of mercerised cotton towards substantive dyes, compare Knecht (*J. Soc. Dyers*, 1908, **24**, 68), and Hübner and Pope (*J. Soc. Chem. Ind.*, 1904, **23**, 401). J. J. S.

Cellulose. II. Hydrocellulose. H. JENTGEN (*Zeitsch. angew. Chem.*, 1911, **24**, 11—12. Compare Abstr., 1910, i, 654).—In support of the view that acid in the molecular condition brings about the conversion of cellulose to hydrocellulose (compare Schwalbe, Abstr., 1910, i, 817), the following facts are given: (1) A 1% aqueous acid solution has practically no hydrolysing effect; (2) Methyl or ethyl alcoholic solutions act slowly, and the action depends on the amount of dissociation; (3) 1% solutions of acids in non-ionising media hydrolyse readily. The compounds of cellulose with the molecular acids are regarded as catalysts. The hydrolysis observed by Schwalbe during acetylation is regarded as a secondary or tertiary process.
J. J. S.

Hydrocellulose. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1911, **24**, 12—13. Compare Abstr., 1910, i, 817).—Mainly polemical in reply to Jentgen (preceding abstract). J. J. S.

Acyl Derivatives of Guanidine. WILHELM TRAUBE (*Ber.*, 1910, **43**, 3586—3590).—Guanidine interacts with the esters of monobasic acids, forming simple acyl guanidines.

Formylguanidine, $NH_2\cdot C(NH)\cdot NH\cdot CHO$, separates in crystalline granules, m. p. 178° (decomp.). On shaking with bromine, *formylbromoguanidine* results; it crystallises in almost colourless needles, which decompose violently at 125°.

Acetylguanidine separates in colourless, rhombic crystals, m. p. 185° to a clear liquid; on further heating, it solidifies, and the new compound, after crystallisation from water, has m. p. 261°. Acetylguanidine hydrochloride has m. p. 145° (Korndörfer found 142°, *Arch. Pharm.*, 1903, **241**, 449).

Chloroacetylguanidine crystallises in slender, colourless needles, m. p. 125°. *Trichloroacetylguanidine* forms small, colourless crystals, m. p. 183°; the *hydrochloride* crystallises in platelets.

Benzoylguanidine forms short, colourless crystals, m. p. 160°; the hydrochloride separates in lustrous needles, m. p. 207° (Korndörfer found 210°, *loc. cit.*).

m-*Nitrobenzoylguanidine* crystallises in stellate needles, m. p. 195—197°. E. F. A.

Complex Salts of Certain Amino-acids. LEO TSCHUGAEFF and E. SERBIN (*Compt. rend.*, 1910, **151**, 1361—1363).—α-Amino-acids form stable, complex, internal salts with certain heavy metals, in

this respect differing from the β-, γ-, and δ-acids, which appear unable to do so. The following salts are sparingly soluble, and were prepared in each case by boiling an aqueous solution of the amino-acid with somewhat less than the calculated amount of purpureochromium chloride.

The *glycine* salt, $Cr\left(<\begin{matrix}NH_2\cdot CH_2\\ O\text{---}CO\end{matrix}\right)_3$, crystallises in small, bright red prisms; it is stable at 300°, and is not decomposed by boiling with alkalis or dilute acids.

The *alanine* salt, $Cr\left(<\begin{matrix}NH_2\cdot CHMe\\ O\text{---}CO\end{matrix}\right)_3$, has a similar constitution, and shows the same properties; it crystallises in rosy needles. The *asparagine* derivative, $Cr(C_4H_7O_3N_2)_3$, is less soluble, and separates in microscopic, rose-violet needles. α-Amino*iso*butyric acid, α-amino*iso*valeric acid, and leucine form similar compounds. The salts can also be prepared, but in a less pure state, by boiling the amino-acids with an aqueous, ammoniacal solution of chromic chloride. When glycine is treated in this way, a basic salt is obtained, for which the constitution $\left(\begin{matrix}CH_2\cdot NH_2\\ CO\text{---}O\end{matrix}>\right)_2Cr<\begin{matrix}OH\\ OH\end{matrix}>Cr\left(<\begin{matrix}NH_2\cdot CH_2\\ O\text{---}CO\end{matrix}\right)_2$, is suggested.

W. O. W.

Action of Carbon Disulphide on Amino-acids. MAX SIEGFRIED and O. WEIDENHAUPT (*Zeitsch. physiol. Chem.*, 1910, 70, 152—160).—Carbon disulphide combines with amino-acids in the presence of barium hydroxide or other alkalis in much the same manner that carbon dioxide does (compare Abstr., 1905, ii, 332; 1906, i, 324; 1908, i, 379), yielding dithiocarboxylic derivatives of the amino-acids; for example, glycol yields a salt of

$$CO_2H\cdot CH_2\cdot NH\cdot CS\cdot SH.$$

Most of the salts are readily soluble, but, when treated with benzyl chloride, yield sparingly soluble acid benzyl esters of the type $CO_2H\cdot CH_2\cdot NH\cdot CS\cdot S\cdot CH_2Ph$, by means of which the dithiocarboxylic acids can be isolated with great ease.

Benzyl hydrogen glycinedithiocarboxylate, $C_{10}H_{11}O_2NS_2$, crystallises from water in long, broad, colourless needles with a silvery lustre, and has m. p. 165°; 100 c.c. of an aqueous solution saturated at the ordinary temperature contains 0·0096 gram of ester. The *barium* salt, $(C_{10}H_{10}O_2NS_2)_2Ba$, crystallises from hot water in broad needles.

The yield of ester is 50% when the theoretical amount (2 mols.) of potassium hydroxide (78·6% solution) is used, but falls to nil when 1·5 times the theoretical amount is used.

Benzyl hydrogen dl-*alaninedithiocarboxylate*,

$$CO_2H\cdot CHMe\cdot NH\cdot CS_2\cdot CH_2Ph,$$

crystallises from water in short, colourless, glistening needles, m. p. 136°. Its solubility at 20° is 0·0102.

Benzyl hydrogen phenylglycinedithiocarboxylate,

$$CO_2H\cdot CH_2\cdot NPh\cdot CS_2\cdot CH_2Ph,$$

crystallises from water in slender needles, m. p. 171°. Its solubility

in water at 20° is 0·0038, and it is only sparingly soluble in hot water.

The acid benzyl ester of *dithiocarboxyphenylaminoacetic acid*, $CO_2H\cdot CHPh\cdot NH\cdot CS_2\cdot CH_2Ph$, crystallises from aqueous alcohol in needles, m. p. 88°; the *barium* salt, $(C_{16}H_{14}O_2NS_2)_2Ba$, crystallises in slender needles.

Benzyl hydrogen sarcosinedithiocarboxylate,

$$CO_2H\cdot CH_2\cdot NMe\cdot CS_2\cdot CH_2Ph,$$

crystallises from hot water in colourless needles, m. p. 125°, and has solubility 0·0153 at 20°. The *barium* salt forms rhombs. *Benzyl hydrogen asparaginedithiocarboxylate*,

$$CO_2H\cdot C_2N_3(CO\cdot NH_2)\cdot NH\cdot CS_2\cdot CH_2Ph,$$

has m. p. 180°, and yields a *barium* salt, which crystallises in slender needles.

Similar compounds have not been obtained from arginine, lysine, histidine, aspartic acid, and glutamic acid; the leucine derivative is oily.

The formation of the sparingly soluble benzyl ester affords a simple method for the separation of glycine from aspartic or glutamic acids. J. J. S.

Syntheses of Bases of the Sugar Group. EMIL FISCHER and KARL ZACH (*Ber.*, 1911, **44**, 132—135).—*Aminomethylglucoside hydrobromide*, $C_7H_{15}O_5N,HBr$, is formed when triacetylmethylglucoside bromohydrin (Fischer and Armstrong, Abstr., 1902, i, 263) reacts with ammonia at the ordinary temperature. The acetyl derivative (10 grams) is sealed up with 12—15 c.c. of solid ammonia. The temperature is allowed to rise gradually to the ordinary temperature, at which it is kept for seven days, and the tube then opened after the ammonia has been again solidified. After removal of the excess of ammonia, the syrup is extracted with absolute alcohol, the alcohol evaporated under reduced pressure, and the residue extracted with warm, dry ethyl acetate, which removes acetamide and leaves a mixture of ammonium bromide and the hydrobromide of the aminoglucoside; the latter is obtained from the mixture in a crystalline form by dissolving in a little warm methyl alcohol and adding much ethyl acetate. To remove the last traces of ammonium bromide, the compound is dissolved in absolute alcohol. The yield is 56% of the theoretical. The salt has not a well-defined m. p., but melts and decomposes at about 205° (corr.). It has $[\alpha]_D^{20}$ $-21\cdot2°$. The *hydrochloride* has m. p. 215° (decomp., corr.) and $[\alpha]_D^{20}$ $-25\cdot1°$, and both salts dissolve readily in water. The free base dissolves in methyl alcohol, but is precipitated as a flocculent mass on the addition of ether. When heated with *N*-hydrochloric acid in a sealed tube at 100°, the hydrochloride yields the salt of an amino-sugar. This reduces Fehling's solution, but is not identical with glucosamine hydrochloride, since it dissolves more readily in water and concentrated hydrochloric acid, and is decomposed much more readily than glucosamine by concentrated hydrochloric acid. The osazone, which it yields with sodium acetate and phenylhydrazine hydrochloride, is not identical with phenylglucosazone. J. J. S.

Preparation of Double Compounds of Carbamide with Alkaline-earth Bromides. GEHE & Co. (D.R.-P. 226224).—The action of carbamide on the alkaline-earth bromides yields compounds of therapeutic value in heart complaints.

Calcium bromocarbamide, m. p. 186°, is prepared by heating calcium bromide (250 parts) with carbamide (225 parts) in the presence of a small quantity of alcohol or water during three hours under a reflux condenser; it crystallises from alcohol or ether.

F. M. G. M.

Preparation of Substituted Carbamic Acid Esters. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 225712).—*α-Methyl-β-trichloroethyl allophanate*, $C_5H_7O_3N_2Cl_3$, prisms, m. p. 186°, is prepared by heating trichloro*iso*propyl alcohol (1 mol.) with carbamic chloride (2 mols.) on the water-bath.

Tetrachloroethyl allophanate, $C_4H_4O_3N_2Cl_4$, is obtained by substituting chloral for the alcohol in the foregoing preparation and allowing the mixture to remain at the ordinary temperature during two days; it forms colourless crystals, which decompose at about 160°. When molecular proportions of trichloro*iso*propyl alcohol and *p*-ethoxyphenylcarbimide are heated together at 185°, *trichloro*iso*propyl* p-*ethoxyphenylcarbamate*, $C_{12}H_{14}O_3NCl_3$, is obtained as a syrup, which after crystallisation from petroleum has m. p. 86°. F. M. G. M.

Preparation of Esters of Allophanic Acid. CHEMISCHE WERKE VORM. DR. HEINRICH BYK (D.R.-P. 226228).—Tertiary alcoholic esters which are therapeutically important are not readily prepared by the ordinary methods, and allophanic tertiary alcoholic esters have not previously been obtained.

Amyl allophanate, $CMe_2Et{\cdot}O{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$, colourless needles, m. p. 149—150°, is prepared by treating a cooled solution of amylene hydrate in an indifferent solvent with cyanic acid and evaporating in a vacuum; it is sparingly soluble in water, ether, or benzene, readily so in alcohol, and is decomposed by hot alkalis. F. M. G. M.

Preparation of α-Bromo-α-ethylbutyrylcarbamide. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 225710).—*α-Bromo-α-ethylbutyrylcarbamide*, $CBrEt_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$, colourless, tasteless, odourless crystals, m. p. 114—118°, and of therapeutic value, is prepared (1) by heating α-bromo-α-ethylbutyryl bromide (obtained by the action of bromine on α-ethylbutyric anhydride) with carbamide at 100°; (2) by the action of sulphuric acid on α-bromoethylbutyrylcyanamide (prepared from cyanamide and α-bromoethylbutyryl chloride); (3) from the interaction of ammonium acetate with *phenyl α-bromo-α-ethylbutyrylcarbamate*, which forms colourless crystals, and is prepared from α-bromo-α-ethylbutyryl bromide and the sodium derivative of phenyl carbamate; (4) by the oxidation of α-bromo-α-ethylbutyrylthiocarbamide with potassium permanganate, or (5) the direct bromination of α-ethylbutyrylcarbamide. F. M. G. M.

Calcium Cyanamide. NIKODEM CARO (*Zeitsch. angew. Chem.* 1910, 23, 2405—2417).—[With B. SCHÜCK]—When solutions contain

ing dicyanodiamide and silver nitrate, in the mol. proportions 1 : 1, 2 : 1, and 3 : 1 are mixed, the compounds $AgNO_3,C_2H_4N_4$, $AgNO_3,2C_2H_4N_4$, and $AgNO_3,3C_2H_4N_4$ are produced. The first of these substances is converted by sodium hydroxide into the compound $C_2H_3N_4Ag$, whilst the second yields a mixture of the same compound and silver oxide.

Silver dicyanodiamide decomposes when boiled, first into silver cyanamide; when the boiling is more prolonged, the latter is further decomposed with production of cyanamide.

Cyanamide, dicyanodiamide, and carbamide are estimated as follows: Calcium cyanamide (7 grams) is shaken for two and a-half hours with 400 c.c. of water, and the solution made up to 500 c.c. A portion of the solution (250 c.c.) is treated with ammonia and silver acetate, diluted to 400 c.c., filtered, and the precipitate washed. The nitrogen (cyanamide) is then estimated by the Kjeldahl method. A part of the filtrate (300 c.c.) is boiled with potassium hydroxide, diluted to 400 c.c., and the nitrogen in the precipitate (dicyanodiamide) estimated as before. A part of the filtrate (300 c.c.) is evaporated down, the silver precipitated with hydrogen sulphide, and the excess of the latter expelled by carbon dioxide. It is then diluted to 400 c.c., and the nitrogen (carbamide) estimated in 100 c.c.

[With RICHARD JACOBY and B. SCHÜCK.]—When calcium carbide is heated in absence of air with 10% sodium cyanide for three hours at 900°, nearly the whole of the cyanide is converted into cyanamide. The same change occurs when barium cyanide is heated in a current of acetylene diluted with hydrogen.

[With B. SCHÜCK.]—When calcium cyanamide is heated in a current of dry carbon dioxide, the carbide present is completely decomposed, and the calcium cyanamide is decomposed with production of carbon.

[With R. JACOBY and B. SCHÜCK.]—As regards the alleged production of nitrides by the action of nitrogen on a mixture of alumina and carbide, it was found that neither nitrides nor cyanamide are produced at 800—1200°, products being obtained containing not more than 0·8% per cent. N at the lower temperature, and generally no nitrogen at temperatures of 1000° or more. Calcium carbide when heated with alumina in an inert atmosphere yields a black substance containing neither calcium nor aluminium carbide.

[With B. SCHÜCK.]—Pure cyanamide can be prepared by slowly adding sodium cyanamide to well cooled, strong hydrochloric acid, and distilling off the water in a vacuum. The cyanamide is then dissolved in ether.

It can also be obtained by adding a concentrated solution of aluminium sulphate to an aqueous extract of calcium cyanamide. The filtrate is distilled in a vacuum and extracted with ether. Cyanamide forms colourless crystals, m. p. 41—42°, readily soluble in water, alcohol, and ether. When heated, it is at once converted into dicyanodiamide (m. p. 204°); the same change takes place when it is exposed to air.

[With R. JACOBY.]—The temperature at which nitrogen acts on mixtures of baryta and carbon is reduced by adding fluorides; the

action takes place at a temperature below the m. p. of the fluoride. When a mixture of barium carbonate, carbon, and calcium (or barium) fluoride is heated without nitrogen at the temperatures employed for nitrogen fixation, there is a production of carbide. No carbide is formed at this temperature in absence of fluoride. N. H. J. M.

Preparation of Phenylnitromethane [ω-Nitrotoluene] by the Action of Mercurous Nitrite on Benzyl Chloride. PAÑCHÁNAN NEOGI and BIRENDRA BHUSAN ADHICÁRY (*Zeitsch. anorg. Chem.*, 1911, 69, 270—272).—ω-Nitrotoluene is readily obtained by the interaction of mercurous nitrite and benzyl chloride, the reaction mixture being fractionally distilled under diminished pressure. The yield is much better than when silver nitrite is used. T. S. P.

Preparation of Diphenylmethane and its Homologues. ERNST VON MEYER (*J. pr. Chem.*, 1910, [ii], 82, 538—540).—The hydrocarbon obtained by the action of phosphoric oxide on benzyl ethyl ether in benzene solution, and regarded by Schickler as an isomeride of stilbene, is shown to be diphenylmethane, not only by the fact that it is not formed when light petroleum is used as the solvent, but also by its oxidation to benzophenone by chromic and acetic acids, and by its nitration to 4 : 4′-dinitrodiphenylmethane and tetranitrodiphenylmethane.

Phenyl-*p*-tolylmethane and phenyl-α-naphthylmethane are obtained in a similar manner by replacing the benzene by toluene and naphthalene respectively; *p*-chlorodiphenylmethane is obtained by using *p*-chlorobenzyl ethyl ether instead of benzyl ethyl ether, and triphenylmethane by employing diphenylmethyl ethyl ether.

C. S.

Triphenylmethyl Chloride, Diphenylcarbamyl Chloride, and Cyanuric Bromide Acting as Acid Halogenides. ERNST VON MEYER (*J. pr. Chem.*, 1910, [ii], 82, 521—538).—A comparative study of transformations in which triphenylmethyl chloride, diphenylcarbamyl chloride, and cyanuric bromide function as acid halogenides.

[With P. FISCHER.]—Triphenylmethyl chloride reacts with carbamide, methylcarbamide, and phenylcarbamide in pyridine to form s-*ditriphenylmethylcarbamide*, $CO(NH{\cdot}CPh_3)_2$, s-*triphenylmethylmethylcarbamide*, $NHMe{\cdot}CO{\cdot}NH{\cdot}CPh_3$, m. p. 263°, and s-*phenyltriphenylmethylcarbamide*, $NHPh{\cdot}CO{\cdot}NH{\cdot}CPh_3$, m. p. 242°, respectively, and with thiocarbamide to form *triphenylmethylthiocarbamide*, $NH_2{\cdot}CS{\cdot}NH{\cdot}CPh_3$, m. p. 217°. Triphenylmethyl chloride reacts with potassium phthalimide at 200° to form *triphenylmethylphthalimide*, $C_6H_4{<}{}^{CO}_{CO}{>}N{\cdot}CPh_3$, m. p. 172°, with pyrrole and with piperidine, yielding *triphenylmethylpyrrole*, $C_4NH_4{\cdot}CPh_3$, m. p. 258°, and *triphenylmethylpiperidine*, $C_5NH_{10}{\cdot}CPh_3$, m. p. 153°, respectively, and with pyridine or quinoline in benzene solution readily forms the crystalline additive compounds, C_5NH_5,CPh_3Cl, m. p. 171°, and C_9NH_7,CPh_3Cl, m. p. 163°, which are decomposed by water or alcohol, and form intensely yellow solutions in hot pyridine. When fused with phenol or with resorcinol, triphenylmethyl chloride yields *p*-hydroxytetraphenylmethane and *dihydroxy-*

tetraphenylmethane, $CPh_3{\cdot}C_6H_4(OH)_2$, m. p. 268°, respectively; with mercaptans in benzene or ethereal solution, however, the chloride acts as an acid chloride, yielding thio-ethers: *triphenylmethyl methyl sulphide*, m. p. 105°, from methyl mercaptan, *triphenylmethyl ethyl sulphide*, m. p. 125°, from ethyl mercaptan, and *phenyl triphenylmethyl sulphide*, m. p. 105°, from phenyl mercaptan. Triphenylmethyl chloride reacts with alcoholic *p*-toluene-sulphinic acid at 130° to form acetaldehyde and triphenylmethane by the decomposition of the initially formed triphenylmethyl ethyl ether, and yields with sodium *p*-toluenesulphinate, in benzene, p-*tolyltriphenylmethylsulphone*, $CPh_3{\cdot}SO_2{\cdot}C_6H_4Me$, m. p. 173°, which is decomposed by water into triphenylcarbinol and *p*-toluenesulphinic acid. Triphenylmethyl chloride reacts in ether with magnesium benzyl chloride to form *triphenylbenzylmethane*, m. p. 140°, with magnesium *p*-chlorobenzyl chloride to form *triphenyl*-p-*chlorobenzylmethane*, m. p. 172°, and with magnesium phenyl bromide to form diphenyl and triphenylmethyl, the latter being obtained in the form of its peroxide.

[With A. NICOLAUS.]—Diphenylcarbamyl chloride and pyridine yield an additive compound, $C_5NH_5,NPh_2{\cdot}COCl$, m. p. 107°, which forms a *platinichloride*, decomp. 170°, *picrate*, m. p. 161°, and *iodide*, m. p. 182°. The formation of esters from diphenylcarbamyl chloride and alcohols only occurs very slowly; easily, however, in the presence of a little alkali or potassium cyanide; ethyl diphenylcarbamate has m. p. 72°, the corresponding *methyl* and iso*propyl* esters, 86° and 117° respectively.

Triphenylsemicarbazide (s-*Diphenylcarbamylphenylhydrazide*),

$$NHPh{\cdot}NH{\cdot}CO{\cdot}NPh_2$$

(*acetyl* derivative, m. p. 165°; *nitroso*-compound, m. p. 131°), is obtained readily from phenylhydrazine (2 mols.) and diphenylcarbamyl chloride in benzene, and is oxidised by alcoholic ferric chloride to *diphenylcarbamylazophenyl*, $NPh{:}N{\cdot}CO{\cdot}NPh_2$, m. p. 138°, red needles, which develops a deep red coloration with concentrated sulphuric acid. The interaction of diphenylcarbamyl chloride and aliphatic amino-acids is accomplished best by employing the latter in the form of their esters or sodium salts, acetone being used as solvents; thus *a-diphenylcarbamidopropionic acid*, $CO_2H{\cdot}CHMe{\cdot}NH{\cdot}CO{\cdot}NPh_2$, m. p. 149°, is obtained from alanine, and *a-diphenylcarbamidohexoic acid*,

$$CH_2Me{\cdot}[CH_2]_2{\cdot}CH(CO_2H){\cdot}NH{\cdot}CO{\cdot}NPh_2,$$

m. p. 52°, from leucine.

Ethyl o-*diphenylcarbamidobenzoate*, $CO_2Et{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NPh_2$, m. p. 108°, obtained by heating equal molecular quantities of ethyl anthranilate and diphenylcarbamyl chloride with an excess of zinc dust at about 100°, yields the free *acid*, m. p. 178°, by hydrolysis. The halogen in diphenylcarbamyl chloride is readily replaced by an alkyl or aryl group by the Grignard reaction; thus with magnesium ethyl iodide it yields *diphenylpropionamide*, m. p. 58°, with magnesium propyl bromide, *diphenylbutyramide*, m. p. 47°, and with magnesium phenyl bromide, *diphenylbenzamide*, m. p. 176°. *Diphenylcarbamyl cyanide*, $NPh_2{\cdot}CO{\cdot}CN$, m. p. 126°, obtained from the chloride and an excess of potassium cyanide at 180—200°, yields diphenylamine, hydrogen cyanide, and carbon dioxide by hydrolysis with alcoholic

potassium hydroxide; it forms an *amido-oxime*, $NPh_2\cdot CO\cdot C(NH_2)\colon NOH$, m. p. 222·5°, with alcoholic hydroxylamine at 60—80°, and is converted in alcoholic solution into the *thioamide*, $NPh_2\cdot CO\cdot CS\cdot NH_2$, m. p. 220°, by hydrogen sulphide in the presence of aqueous ammonia.

[With FRAULEIN NÄBE.]—Cyanuric bromide is obtained in 70—80% yield by the action of nascent hydrogen bromide on a benzene solution of cyanogen bromide. Cyanuric bromide forms cyanuric trihydrazide with 10% hydrazine, cyanuric triphenylhydrazide with ethereal phenylhydrazine, and in boiling benzene reacts (*a*) with *o*-chloroaniline to form *cyanuric tri-*o*-chloroanilide* (*trichlorophenylmelamine*),

$$(CN)_3(NH\cdot C_6H_4Cl)_3,$$

m. p. 161°; (*b*) with 2:4-dichloroaniline to form *cyanuric tri-2:4-dichloroanilide*, m. p. 261°; (*c*) with *m*-nitroaniline to form *trinitrophenylmelamine*, $(CN)_3(NH\cdot C_6H_4\cdot NO_2)_3$; (*d*) with α-naphthylamine to form *tri-α-naphthylmelamine*, $(CN)_3(NH\cdot C_{10}H_7)_3$, m. p. 225°; (*e*) with methylaniline to form *triphenyltrimethylmelamine*, $(CN)_3(NMePh)_3$, m. p. 115°; (*f*) with benzylaniline to form *triphenyltribenzylmelamine*, m. p. 120°; (*g*) with *p*-aminophenol to form *cyanuric di-*p*-hydroxyanilide bromide*, $(CN)_3(NH\cdot C_6H_4\cdot OH)_2Br$, m. p. 275° (decomp.); (*h*) with *p*-anisidine to form a corresponding *anisidide*,

$$(CN)_3(NH\cdot C_6H_4\cdot OMe)_2Br,$$

m. p. 250° (decomp.), and (*i*) with anthranilic acid to form the *substance*, $(CN)_3(NH\cdot C_6H_4\cdot CO_2H)_2Br$, m. p. 197°. Cyanuric bromide and carbamide (3 mols.) at 130—140° yield *tricarbamylmelamine*,

$$(CN)_3(NH\cdot CO\cdot NH_2)_3,$$

m. p. above 300°.

Cyanuric bromide reacts in the normal way with aluminium chloride and an aromatic hydrocarbon in the presence of carbon disulphide, forming substances of the type: $(CN)_3Ar_3$; Ar = Ph, m. p. 231°; Ar = p-C_6H_4Me, m. p. 275—276°; Ar = 3:4-$C_6H_3Me_2$, m. p. 210°; Ar = 2:4-$C_6H_3Me_2$, m. p. 155°; Ar = p-$C_6H_4\cdot OMe$, m. p. 115°; Ar = α-$C_{10}H_7$, m. p. 190—200°; the constitutions of these compounds (excluding the first) are determined by the fact that hydrolysis by hydrochloric acid at 200—220° yields *p*-toluic, 3:4-dimethylbenzoic, 2:4-dimethylbenzoic, anisic, and α-naphthoic acids respectively. The analogous triethyl compound, $(CN)_3Et_3$, obtained by Otto and Voigt from dichloropropionitrile is also produced by the interaction of cyanuric bromide and ethereal magnesium ethyl iodide. C. S.

Triarylmethyls. V. WILHELM SCHLENK and ANNA HERZENSTEIN (*Ber.*, 1910, **43**, 3541—3546. Compare Abstr., 1909, i, 791; 1910, i, 236, 237, 469).—According to the authors, the sole objection to the hexaphenylethane formula for the colourless form of triphenylmethyl lies in the comparative stability of the closely related pentaphenylethane. Investigation of the behaviour of the latter compound in high boiling solvents shows, however, that the remarkable power of dissociation characteristic of "colourless" triphenylmethyl is also shared by pentaphenylethane, although in a less marked degree.

Solutions of pentaphenylethane in anisole or ethyl benzoate, on being heated rapidly to boiling, acquire the deep yellowish-brown colour of a hot solution of triphenylmethyl; on quickly cooling, the colour

diminishes to a light yellow. The solution decolorises iodine, and at once becomes colourless when shaken with air; the colour, however, rapidly reappears, and finally vanishes only by repeated shaking with air. This behaviour so closely resembles that of triphenylmethyl solutions that there can be no doubt that triphenylmethyl is one of the products of dissociation of pentaphenylethane, $Ph_3C{-}|{-}CHPh_2$. The second dissociation product, diphenylmethyl, polymerises to tetraphenylethane, which can be readily isolated by boiling pentaphenylethane in ethyl benzoate solution in an atmosphere of nitrogen.

On passing oxygen through a boiling solution of pentaphenylethane in ethyl benzoate, the diphenylmethyl is oxidised to tetraphenylethylene.

A new method of formation of hexa-arylethanes is also described. When a concentrated benzene solution of molecular quantities of 4-phenyl-triphenylmethane and 4-phenyl-triphenylmethyl chloride is exposed to sunlight, it acquires a reddish colour, due to the formation of 4-phenyl-triphenylmethyl: $C_6H_4Ph{\cdot}CPh_2H + ClCPh_2{\cdot}C_6H_4Ph \rightleftharpoons C_6H_4Ph{\cdot}CPh_2{\cdots}CPh_2{\cdot}C_6H_4Ph + HCl$.

The reaction is, however, reversible, the amount of 4-phenyl-triphenylmethyl being very small when equilibrium is attained.

In a similar manner phenylbisdiphenylmethyl, $CPh(C_6H_4Ph)_2$, is obtained from phenylbisdiphenylmethane and phenylbisdiphenylmethyl chloride.

Diphenylbisdiphenylene-ethane, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>\!CPh{\cdot}CPh\!<\!\!\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$, on account of its stability towards hydrochloric acid, is produced in quantitative yield by exposing a concentrated benzene solution of phenyldiphenylene-methyl chloride and phenyldiphenylenemethane (phenylfluorene) to the action of sunlight. F. B.

Hydrogenations in Presence of Palladium. Applications to Phenanthrene. Pierre Breteau (*Compt. rend.*, 1910, **151**, 1368—1369).—By passing a mixture of phenanthrene vapour and hydrogen over spongy palladium at 160°, a mixture of the tetra- and octa-hydride is obtained; when hydrogenation is carried out at the ordinary temperature, in presence of palladium black suspended in *cyclo*hexane, only the tetrahydride is formed. Precipitated palladium, prepared by treating a solution of the chloride in hydrochloric acid with zinc, also yields the tetrahydride when brought into contact with phenanthrene in alcoholic solution. W. O. W.

Action of Concentrated Sulphuric Acid on Some Aromatic Nitroamines. II. Derivatives of Methylaniline, Methyl-*p*-anisidine, and Methyltoluidines. Frédéric Reverdin (*Bull. Soc. chim.*, 1911, [iv], **9**, 43—49. Compare Abstr., 1910, i, 255).—Further instances are given of the reduction of the nitro- to the nitroso-group by sulphuric acid in certain aromatic nitro-derivatives, and it is shown that this reaction explains why such nitro-derivatives respond to Liebermann's test.

2 : 4 : 6-Trinitrophenylmethylnitroamine, on treatment with sulphuric acid at atmospheric temperature, furnishes picramide and some nitrosomethylpicramide (Bamberger and Müller, Abstr., 1900, i, 217). The latter is also produced if alcohol is used along with sulphuric acid,

but in this case the principal product of the reaction is trinitromethylaniline.

Dimethyl-*p*-anisidine, on nitration in the cold, furnishes the N-*nitroso*-derivative of dinitromethyl-*p*-anisidine, m. p. 111—112°, but with hot nitric acid gives the N-*nitro*-derivative, m. p. 125°, which may also be obtained by the further action of nitric acid on the nitrosoamine, and, conversely, the latter is reproduced by the action of sulphuric acid on the nitroamine. Further, when the nitroamine is heated with phenol or the nitrosoamine is heated with hydrochloric acid, *dinitromethyl*-p-*anisidine*, m. p. 129°, is formed. By boiling the nitroamine with sodium hydroxide solution, a small yield of Weselsky and Benedikt's dinitroquinol methyl ether (Abstr., 1881, 1139) is obtained. The fact that this nitroamine, like that obtained from dimethyl-*o*-anisidine (Abstr., 1910, i, 255), gave the Liebermann reaction, led the author to examine nitroamines obtained from alkyltoluidines, and for this purpose 3 : 5-dinitro-*o*-tolylmethylnitroamine and its *p*-isomeride were prepared by the method described by van Romburgh (*Rec. trav. chim.*, 1884, 3, 392). As secondary products in these preparations some 3 : 5-dinitro-2-nitromethylaminobenzoic acid and its 4-isomeride were obtained (Abstr., 1908, i, 167). These melted at 187° and 204° respectively. Both nitroamines gave Liebermann's reaction. The first on treatment with sulphuric acid at atmospheric temperature gives Stoermer's 3 : 5-dinitro-*o*-tolylmethylnitrosoamine (Abstr., 1899, i, 44), but is recovered unchanged from sulphuric acid at −10°. 3 : 5-Dinitro-*o*-tolylmethylnitroamine, with sulphuric acid at atmospheric temperature, furnishes 3 : 5-dinitro-2-nitromethylaminobenzoic acid (see above) and a *substance* crystallising in colourless needles and decomposing above 300°, but with sulphuric acid at −10° it gives the same acid with, as chief product, 3 : 5-dinitro-*p*-tolylmethylnitrosoamine, m. p. 127—128° (compare van Romburgh, Abstr., 1896, i, 478). T. A. H.

The Reaction of Cellulose Nitrate with Dimethylaniline. JOHANN WALTER (*Zeitsch. angew. Chem.*, 1911, 24, 62—64).—Guncotton and celluloid absorb dimethylaniline, the colour gradually deepening through green and blue to violet. The coloration becomes darker on exposure to light, and is not removed by solvents. Strongly-coloured specimens have an odour of phenylmethylnitrosoamine. Other aromatic amines produce similar colorations, but less rapidly and of less intensity. C. H. D.

Velocities of Addition of Bromine to the Imides of Some Substituted Maleinamic Acids. II. ARNALDO PIUTTI and G. CALCAGNI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1910, [iii], 16, 255—261. Compare Abstr., 1909, i, 360).—Continuing their investigations on this subject, the authors have measured the velocities of addition of bromine to the following imides (compare Abstr., 1910, i, 672): hydroxyphenylmaleinimide (white form), methoxyphenylmaleinimide (white and yellow forms), ethoxyphenylmaleinimide (white and yellow forms). The velocity is very slow in all these cases; for the white imides, the reaction is complete in about fifty days, for the yellow forms in about seventy-five days. Since Bauer has shown that

substance of this type the power of adding on bromine diminishes with increase in the number of negative groups, this forms an additional argument for assigning to the yellow form the symmetrical formula $\begin{matrix} CH\cdot CO \\ \Vert \\ CH\cdot CO \end{matrix}\!\!>N\cdot C_6H_4\cdot OR$. The white isomerides behave as weak bases, and that is consonant with their having the constitution $\begin{matrix} CO\text{—}O \\ | \\ CH:CH \end{matrix}\!\!>C:N\cdot C_6H_4\cdot OR$. R. V. S.

Preparation of Alkali and Ammonium Salts of Nitrosoarylhydroxylamines. OSKAR BAUDISCH (D.R.-P. 227659).—Nitrosoarylhydroxylamines are known, but their salts have not previously been obtained; they are now prepared by either the oxidation of an amine or the reduction of a nitro-compound in alkaline solution in the presence of sodium nitrite, or an alkyl nitrite.

Ammonium nitrosophenylhydroxylamine, prepared from nitrobenzene, concentrated ammonium hydroxide, zinc dust, and amyl nitrite, crystallises in silvery leaflets, m. p. 163—164°, and sublimes readily.

The *sodium* salt, $C_6H_5\cdot N(NC)\cdot ONa$, and the *potassium* salt form snow-white needles; the *iron* salt crystallises in garnet-red needles or rosettes, with a blue, metallic lustre; it is insoluble in water, but soluble in the ordinary organic solvents; the *copper* salt forms dark grey crystals, and has similar properties. *Ammonium α-nitrosonaphthylhydroxylamine*, colourless leaflets, is rather unstable, turning pink in the light; it dissolves in water, and is converted on boiling into α-nitrosonaphthalene; the *sodium* and *potassium* salts are colourless; the *copper* salt, $(C_{10}H_7O_2N_2)_2Cu$, forms glistening, bluish-grey needles insoluble in water.

The formation of complex double salts of ammonium with copper, nickel, cobalt, or iron is also discussed. F. M. G. M.

Separation of *p*- and *m*-Nitro-*o*-anisidine. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 228357).—The nitration of aceto-*o*-anisidide yields a mixture of two isomeric nitroaceto-*o*-anisidides; these have previously been separated by the more ready hydrolytic dissociation of *p*-nitro-*o*-anisidine, which is precipitated by the addition of water to an acid solution of the mixed sulphates, whilst *m*-nitro-*o*-anisidine sulphate remains in solution.

It is now found that a separation can be effected by fractional crystallisation of the mixed sulphates; the mixture of *m*- and *p*-nitroaceto-*o*-anisidides is hydrolysed by heating with 70% sulphuric acid, and the mixture then diluted with hot water until the concentration of the sulphuric acid is reduced to 40%; on cooling, pure *p-nitro-o-anisidine sulphate* separates in colourless crystals, and the *m*-nitro-*o*-anisidine is precipitated from the filtrate by the addition of alkali.

F. M. G. M.

Preparation of Phenyl Ortho-oxalates. SCHÜLKE and MAYR (D.R.-P. 226231).—When dehydrated oxalic acid is mixed with fused

phenol (2 mols.) at a temperature of about 40°, and then heated to 90—100° with continual stirring, pure *diphenyl ortho-oxalate*,

$$OPh\cdot C(OH)_2\cdot C(OH)_2\cdot OPh,$$

is obtained in quantitative yield; it crystallises from acetic acid, and has m. p. 126°. F. M. G. M.

Synthesis of Alcohols in the *cyclo*Hexane Series. ALPHONSE MAILHE and MARCEL MURAT (*Bull. Soc. chim.*, 1910, [iv], 7, 1083—1089). —The condensation of 1-methyl*cyclo*hexan-3-one with various magnesium alkyl haloids has been studied, and the alcohols obtained, and some of their derivatives are described (compare Sabatier and Mailhe, Abstr., 1906, i, 254; Murat, Abstr., 1909, i, 146).

1-Methyl-3-ethyl*cyclo*hexan-3-ol, D^0 0·9201, D^{20} 0·9013, n_D 1·459, b. p. 88°/20 mm., obtained by condensing 1-methyl*cyclo*hexan-3-one (Abstr., 1905, i, 275) with ethyl magnesium bromide, is a colourless liquid, with a feebly camphoraceous odour (compare Zelinsky, Abstr., 1901, i, 661); the *phenylurethane*, m. p. 98°, crystallises in colourless prisms; the *acetate*, D^0 0·9493, D^{20} 0·9303, n_D 1·441, b. p. 98—100°/20 mm., has a fruity odour. The alcohol is readily dehydrated, yielding 1-*methyl*-3-*ethyl*cyclo*hexene*, D^0 0·8366, D^{20} 0·8296, n_D 1·454, b. p. 149—151°/760 mm., a mobile, colourless liquid of pleasant odour; it gives a greenish coloration with sulphuric acid and alcohol, furnishes a *nitrosochloride*, m. p. 124—126°, and on reduction yields 1-*methyl*-3-*ethyl*cyclo*hexane*, D^0 0·8320, D^{20} 0·8213, n_D 1·460, b. p. 145—146°. 1-Methyl-3-propyl*cyclo*hexan-3-ol, D^0 0·9063, D^{15} 0·8961, n_D 1·461, b. p. 96—98°/20 mm., is a colourless, viscous liquid (Zelinsky, *loc. cit.*); it yields a *phenylurethane*, m. p. 112°, and an *acetate*, D^0 0·9367, D^{20} 0·9248, n_D 1·454, and b. p. 108—110°/20 mm., which is colourless and has a fruity odour. The alcohol is readily dehydrated, yielding 1-*methyl*-3-*propyl*cyclo*hexene*, D^0 0·8375, D^{15} 0·8302, n_D 1·456, and b. p. 168—171°/760 mm., which absorbs bromine and gives a yellowish-green colour with alcohol and sulphuric acid, furnishes a *nitrosochloride*, m. p. 128—131° (decomp.), and on reduction gives 1-*methyl*-3-*propyl*cyclo*hexane*, b. p. 164—165°.

1-*Methyl*-3-iso*butyl*cyclo*hexan*-3-*ol*, D^0 0·9011, D^{19} 0·8972, n_D 1·465, b. p. 107—109°/20 mm., is best obtained by condensing magnesium *iso*butyl chloride with methyl*cyclo*hexanone, although the secondary reaction already described (Abstr., 1905, i, 706) occurs and occasions some loss. The alcohol is viscous and dehydrates easily, giving an *ethylenic hydrocarbon*, b. p. 192—195°, having a somewhat alliaceous odour.

1-*Methyl*-3-iso*amyl*cyclo*hexan*-3-*ol*, D^0 0·8982, D^{22} 0·8856, n_D 1·464, b. p. 126—127°/20 mm., is a viscous, colourless, pleasant-smelling liquid; the *phenylurethane*, m. p. 128°, is crystalline, and the *acetate*, D^{20} 0·9146, n_D 1·457, b. p. 140°/20 mm., is a thick liquid with a pleasant odour. The alcohol on dehydration gives 1-*methyl*-3-iso*amyl*cyclo*hexene*, D^0 0·8301, D^{20} 0·8190, n_D 1·459, b. p. 209—211°/760 mm., which gives a greenish coloration with sulphuric acid and alcohol, yields a *nitrosochloride*, m. p. 136°, and on reduction furnishes 1-*methyl*-3-iso*amyl*cyclo*hexane*, b. p. 205°, a colourless liquid with an odour recalling that of petrol.

3-cyclo*Hexyl*-1-*methyl*cyclo*hexan*-3-*ol*, D^0 0·9815, D^{18} 0·9685, n_D 1·495, b. p. 153—155°/20 mm., is a viscous liquid of agreeable aroma, yields a *phenylurethane*, m. p. 141°, gives an intense blue coloration with bromine in chloroform, and on dehydration furnishes 3-cyclo*hexyl*-1-*methyl*cyclo*hexene*, D^0 0·9634, D^{18} 0·9138, n_D 1·492, b. p. 240°/760 mm., a mobile liquid which is scarcely coloured by sulphuric acid and alcohol, but gives a *nitrosochloride*, m. p. 142—146°, which is possibly a mixture of isomerides.

3-*Phenyl*-1-*methyl*cyclo*hexan*-3-*ol*, m. p. 61°, b. p. 153°/20 mm. (decomp.), crystallises in monoclinic prisms, yields a *phenylurethane*, m. p. 143°, and on dehydration furnishes 3-*phenyl*-1-*methyl*cyclo*hexene*, D^0 0·9859, D^{20} 0·9702, n_D^{20} 1·555, and b. p. 145°/20 mm., as a colourless, mobile liquid, which absorbs bromine, and with sulphuric acid and alcohol gives a rose-red coloration.

3-*Benzyl*-1-*methyl*cyclo*hexan*-3-*ol*, D^0 1·0032, D^{17} 0·9873, n_D 1·532, b. p. 165°/18 mm. (decomp.), is a colourless liquid, having a lemon-like odour, and is obtained in small yields by condensing methyl*cyclo*hexanone with benzyl magnesium chloride, the chief product being dibenzyl. 3-*Benzyl*-1-*methyl*cyclo*hexene*, D^0 0·9693, D^{20} 0·9591, n_D 1·547, b. p. 156°/20 mm. or 271°/760 mm., is colourless, and has a disagreeable odour. T. A. H.

A Solid Molecular Compound of Hexamethylenetetramine and Guaiacol. F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 225924).—The preparation of a hexamethylenetetraminetriguaiacol has been previously described (Abstr., 1910, i, 378). A compound obtained in a similar manner and with identical properties is now found to have tho composition of a hexamethylenetetraminediguaiacol, and it is suggested that the former compound was possibly not an individual substance. F. M. G. M.

Fermentation of Tyrosine to *p*-Hydroxyphenylethanol (Tyrosol). FELIX EHRLICH (*Ber.*, 1911, 44, 139—146. Compare Abstr., 1907, ii, 384).—A 60—80% yield of *p*-hydroxyphenylethanol, $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot OH$, can be obtained by the fermentation of tyrosine with large amounts of yeast in the presence of much sugar and of nutritive salts. Small amounts of acids are also formed; these are soluble in ether, and give Millon's reaction. The hydroxy-alcohol is termed *tyrosol*. It crystallises in long, glistening needles and rods of rhombic habit; it has m. p. 93° and b. p. 310°. It has a bitter taste, does not reduce Fehling's solution, and gives a Bordeaux-red coloration when warmed with concentrated sulphuric acid. With ferric chloride solution it gives an indigo-blue coloration, and with Millon's reagent, and also with diazobenzenesulphonic acid, dark red colorations. It does not give the Piria reaction, but develops an intense yellowish-green coloration with formaldehyde and sulphuric acid. It is oxidised by alkaline permanganate solutions, reacts with phosphorus pentachloride, yielding a yellow oil, and also forms an oily acetyl derivative. The *dibenzoyl* derivative, $C_{22}H_{18}O_4$, prepared by the Schotten-Baumann method, crystallises from alcohol in felted needles, m. p. 111°.

The formation of tyrosol is brought about by either top or bottom

yeasts. It is also formed in appreciable amounts when a sterilised solution of tyrosine and sugar is inoculated with pure cultures of yeast, and in small amounts during the fermentation of pure sugar solutions by pure yeasts. Its formation in the latter case is due to the autolysis of the dead yeast cells and the formation of tyrosine, which is used as nitrogenous nutritive material by the living cells and transformed into tyrosol. It is not formed in the absence of sugars.

Tyrosol thus appears to be a by-product in most processes of fermentation by yeast, and is present in all fermented liquors, especially in beer and wine, the flavours of which are due, in part, to the presence of the hydroxy-alcohol. J. J. S.

Preparation of Nitrobenzoic Acids from the Corresponding Nitrotoluenes. GUSTAV LÜTTGEN (D.R.-P. 226225).—The oxidation of nitrotoluenes to the corresponding nitrobenzoic acids with nitric and sulphuric acids is not satisfactory; it is now found that the reaction proceeds smoothly in nitric acid solution with potassium chlorate as the oxidising agent. 2 : 4 : 6-Trinitrotoluene was dissolved in concentrated nitric acid (48 Bé), and warmed to 90—95°; potassium chlorate (2 parts) was gradually stirred in, the temperature being maintained meanwhile at 100—120°; pure trinitrobenzoic acid separated from the reaction mixture on cooling. F. M. G. M.

Synthesis of Compounds of the Normal Amyl Series from Piperidine. JULIUS VON BRAUN and W. SOBECKI (*Ber.*, 1910, **43**, 3596—3599).—Although benzo-ε-chloroamylamide, derived from piperidine, is very stable, the corresponding benzoiodoamylamide is relatively easily reduced. It is prepared from the chloro-compound by boiling this with sodium iodide in alcohol, and is dissolved in much concentrated hydrochloric and acetic acid, cooled, and stirred with zinc dust for a number of hours.

Benzo-n-*amylamide* separates as an oil, and is purified by distillation; b. p. 208—210°/15 mm. It is readily hydrolysed to *n*-amylamine, or when distilled with phosphorus pentachloride or pentabromide is converted into *n*-amyl chloride or bromide respectively. To prove that the normal carbon-chain structure had remained intact, the bromide was boiled with potassium cyanide and converted into the nitrile of *n*-hexoic acid. E. F. A.

Secondary Anthranilic Acids and the Transformation of their Nitroso-derivatives into a Peculiar Class of Intensely Red Substances, Soluble in Water. JOSEF HOUBEN and TH. ARENDT (*Ber.*, 1910, **43**, 3533—3541. Compare Abstr., 1908, i, 27; 1909, i, 645, 794).—Previous attempts to nitrosylate methyl dimethylanthranilate failed. The authors now find that the action of sodium nitrite and fuming hydrochloric acid on the ester yields 5-nitroso-*N*-methylanthranilic acid, one of the methyl groups being split off from the nitrogen atom.

When 5-nitroso-*N*-methylanthranilic acid is dissolved in sodium carbonate and shaken with acetic anhydride, a red substance is formed,

which is very soluble in water. Similar red products have been obtained by the action of various acid chlorides and anhydrides, either in aqueous or pyridine solution, on a large number of nitroso-derivatives of secondary anthranilic acids and their esters, and also on quinoneoximecarboxylic acid, but only in one instance has the product been isolated.

When 5-nitroso-*N*-methylanthranilic acid is shaken with pyridine and acetic anhydride, a red solution is formed, from which, by the addition of ether, a brownish-red *pyridine* salt, $C_{15}H_{15}O_4N_3$, is precipitated; the salt is very soluble in water, forming blood-red solutions, and melts with decomposition to a dark red liquid.

[With L. ETTINGER.]—N-*Acetonylanthranilic acid*,

$$CO_2H \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot COMe,$$

prepared by dissolving anthranilic acid in the equivalent quantity of potassium carbonate and boiling the solution with chloroacetone, has m. p. 169—170°; the *nitrosamine*, which forms white crystals, m. p. 115—116° (decomp.), could not be transformed into 5-nitroso-*N*-acetonylanthranilic acid by the action of hydrochloric acid; the *semicarbazone*, $CO_2H \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CMe{:}N \cdot NH \cdot CO \cdot NH_2$, obtained from the *sodium bisulphite* compound of acetonylanthranilic acid, has m. p. 240—241° (decomp.).

Methylacetonylanthranilic acid, $CO_2H \cdot C_6H_4 \cdot NMe \cdot CH_2 \cdot COMe$, prepared from methylanthranilic acid and chloroacetone, crystallises in small, light grey needles, m. p. 123—126°.

2 : 4-*Dinitrodiphenylmethylamine-2′-carboxylic acid*,

$$CO_2H \cdot C_6H_4 \cdot NMe \cdot C_6H_3(NO_2)_2,$$

is obtained by boiling 4-chloro-1 : 3-dinitrobenzene with methylanthranilic acid in aqueous potassium carbonate; it forms clusters of yellow needles, m. p. 178°. F. B.

Action of Ethereal Salts on the Monosodium Derivative of Phenylacetonitrile. F. BODROUX (*Compt. rend.*, 1910, **151**, 1357—1359. Compare Abstr., 1910, i, 623).—Ethyl benzoate condenses with the sodium derivative of phenylacetonitrile to give a 75% yield of cyanophenylacetophenone, $CN \cdot CHPh \cdot COPh$, lamellæ, m. p. 93—94° (compare Walther and Schickler, Abstr., 1897, i, 522). Ethyl carbonate in the same way forms ethyl cyanophenylacetate, $CN \cdot CHPh \cdot CO_2Et$, b. p. 163—165°/19 mm., D^{17} 1·085, the yield being 55%. Ethyl oxalate yields a small quantity of ethyl cyanophenylpyruvate. The foregoing cyano-derivatives are sufficiently acidic to be capable of titration, using phenolphthalein as indicator.

W. O. W.

Crystallographic Examination of Some Nitrophenylmethylacrylic Derivatives. FRANCESCO RANFALDI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1910, [iii], 16, 225—234).—β-*o*-Nitrophenyl-α-methylacrylic acid, $NO_2 \cdot C_6H_4 \cdot CH{:}CMe \cdot CO_2H$, forms monoclinic, prismatic crystals [$a : b : c = 1·3446 : 1 : 1·4562$; $\beta = 92°24'51''$]. β-*m*-Nitrophenyl-α-methylacrylic acid forms colourless, acicular crystals, which could not be obtained in a measurable form. β-*p*-Nitrophenyl-α-methylacrylic acid forms triclinic, pinacoidal crystals [$a : b : c = 1·2867 : 1 : 1·4602$; $\alpha = 84°42'8''$; $\beta = 83°31'31''$, $\gamma = 87°35'18''$]. Sodium β-*o*-nitrophenyl-

α-methylacrylate forms rhombic, disphenoidal crystals [$a:b:c = 1.3940:1:2.0544$]. R. V. S.

Preparation of Glycol Monosalicylate. C. F. Boehringer & Söhne (D.R.-P. 225984. Compare Abstr., 1908, i, 176).—The esterification of salicylic acid with ethylene chlorohydrin yields *β-chloroethyl salicylate*, $OH\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2Cl$, which on careful hydrolysis with mild reagents gives the therapeutically valuable *glycol salicylate*, $OH\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot OH$.

The hydrolytic agents described as suitable are (1) sodium acetate and dilute acetic acid; (2) disodium phosphate and water, or (3) sodium salicylate and water, a sealed tube being employed and a temperature of 130° maintained in each case. F. M. G. M.

Pyrogenetic Decomposition of *cyclo*Gallipharic Acid. Hermann Kunz-Krause and Paul Manicke (*Arch. Pharm.*, 1910, **248**, 695—709. Compare Abstr., 1904, i, 587; 1910, i, 458, 677).—The decomposition of *cyclo*gallipharic acid when heated alone or with various dehydrating agents has been studied, and the results correlated with those recorded in previous papers (*loc. cit.*).

When heated with potassium hydrogen sulphate, the acid furnishes unsaturated gaseous hydrocarbons, acraldehyde, *cyclo*gallipharol, and 4-hydroxy-*m*-xylene.

Sulphuric acid is without action on *cyclo*gallipharic acid in the cold, but on heating with this reagent, it is converted into the keto-anhydride of *cyclo*gallipharic acid at 125—130°; at 150—160° some *cyclo*gallipharol is formed, and at 180° this substance is the sole product of the reaction.

When heated alone, the temperature being gradually raised from 130° to 250°, the amounts of carbon dioxide evolved indicate that the acid undergoes the same progressive decomposition as with sulphuric acid, the same stages, however, being reached at somewhat higher temperatures. Above 250° complete decomposition into carbon dioxide and volatile hydrocarbons takes place. In conclusion, a summary of the results recorded in this and the two preceding papers of the series is given. T. A. H.

Preparation of Carvacrolphthalein. Curt Ehrlich (D.R.-P. 225983).—*Carvacrolphthalein*, colourless, transparent needles, m. p. 246—247°, is prepared by heating phthalic anhydride (1 part) with carvacrol (2 parts) and stannic chloride (2 parts) at 100° during two hours. It is insoluble in water, soluble in sodium hydroxide with a deep blue colour, and compares very favourably with phenolphthalein as an indicator. F. M. G. M.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXIII. Trimellitic Acid. Rudolf Wegscheider, Heinrich Felix Perndanner, and Otto Auspitzer (*Monatsh.*, 1910, **31**, 1253—1301).—The formation of acid esters of trimellitic acid (benzene-1:2:4-tricarboxylic acid) by different methods has been studied in order to determine whether the rules previously laid down for dibasic acids

hold good. The investigation was complicated by the fact that the three carboxyl groups differ but little from one another, and therefore mixtures of acid esters are obtained by each method; these mixtures cannot be separated readily into their constituents. They do not crystallise well, and several of them tend to form mixed crystals. The 1 : 4- and 2 : 4-dimethyl esters crystallise extremely slowly, and are usually obtained as syrups, although from their constitutions their m. p.'s should be relatively high. The constitution of the 4-methyl ester,

$CO_2Me\cdot C_6H_3\cdot(CO_2H)_2$ $[(CO_2H)_2\colon CO_2Me = 1:2:4]$,

follows from the fact that it is formed by the addition of water to the methyl ester of the anhydro-acid, $CO_2Me\cdot C_6H_3\colon(CO)_2O$, and the constitutions of the two isomeric monomethyl esters were determined by conversion into the corresponding amidedicarboxylic acid and then by means of bromine and potassium hydroxide, transforming the amides into amino*iso*- and aminotere-phthalic acids. The constitution of the dimethyl esters was determined by the elimination of carbon dioxide from their potassium salts in the presence of lime.

The products formed by the esterification of the acid, both by the direct and by the catalytic method, could not be obtained pure, with the exception of small amounts of the 1- and 2-monomethyl esters, but the fact that the syrups obtained yield appreciable amounts of the methyl ester of anhydrotrimellitic acid points to the conclusion that by these methods the carboxyl groups in position 4, that is, the carboxyl group least affected by "steric hindrance," is first esterified. The 1- and 2-monomethyl esters, under similar conditions, yield the 1 : 4- and 2 : 4-dimethyl esters, and but little 1 : 2-dimethyl ester. By partial hydrolysis of the normal ester with potassium hydroxide, the 1 : 2-dimethyl ester is first formed, and, by further hydrolysis, the 2-monomethyl ester, with smaller amounts of the isomeric 1-ester. By the addition of methyl alcohol to the acid anhydride, both the 1- and 2-monomethyl esters are formed, but, at the same time, the carboxylic group in position 4 is esterified to a slight extent. The mono-silver salt with methyl iodide yields mainly 1-methyl, together with the 2-methyl ester, and the disilver salt yields mainly 1 : 2-dimethyl ester. These results agree on the whole with the generalisation that in the formation of acid esters from the acid by esterification, or from neutral esters by hydrolysis, steric hindrance is the determining factor, whereas in the formation from the anhydride or from the acid metallic salts, the relative strengths of the carboxyl groups are of first importance.

Full details of the methods used for separating the mixtures obtained in each experiment are given.

Methyl hydrogen *iso*phthalate has m. p. 167—169°, and not 126° as stated by Meyer (*Monatsh.*, 1901, **22**, 437).

A 20% yield of trimellitic acid can be obtained by the action of nitric acid on French colophony (compare Scheder, *Ann. Chem. Pharm.*, 1874, **172**, 94), provided the mother liquors are worked up. It has not been found possible to prepare the acid from naphthol yellow-*S* by Rée's method (Trans., 1886, **49**, 510), but Schultz' method (Abstr., 1909, i, 897) gives fairly good yields if the chromic anhydride is added

gradually. The m. p. depends on the method of heating; when dipped into a bath at 200°, it has m. p. 215—217° in an open tube or 229—234° in a closed tube. A 2% solution of the normal ammonium salt gives precipitates with solutions of mercuric, cadmium, lead, ferric, aluminium, uranyl, and silver salts.

The following acid salts have been prepared: $CO_2H{\cdot}C_6H_3(CO_2Ag)_2$, slender needles from hot water; $CO_2Ag{\cdot}C_6H_3(CO_2H)_2$; $C_9H_4O_6Ba,H_2O$, insoluble in water.

The 1-*monomethyl* ester, $C_{10}H_8O_6$, is most readily prepared from the mono-silver salt, and is most conveniently separated from the free acid by precipitating the latter in the form of its barium salt; it may be purified by the addition of benzene to its ethereal solution, and has m. p. 203·5—205·5°, but frequently melts to a certain extent at 177°, resolidifies at 179°, and then melts at the higher temperature given. The two m. p.'s are probably due to dimorphism. When mixed with the isomeric 2-*monomethyl* ester, its m. p. is not appreciably affected. The latter ester is best prepared by the partial hydrolysis of the 1 : 2-dimethyl ester; it is sparingly soluble in water, whereas the 1-ester dissolves readily, and crystallises from this medium as a colourless powder, m. p. 208°. The 4-methyl ester is most readily obtained by the addition of water to the methyl ester of the anhydro-acid, and crystallises from water in compact plates, m. p. 145—147°. The *anhydro*-ester, $CO_2Me{\cdot}C_6H_3{<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}O$, has m. p. 94—99°, is transformed into a syrup by the addition of a little alcohol, and when kept for some time, even in a desiccator, yields the 4-monomethyl ester. The 1 : 2-*dimethyl* ester, $C_{11}H_{10}O_6$, crystallises from carbon tetrachloride, or better from a mixture of ether and light petroleum, in nodular masses of needles, m. p. 115·5—117° after softening at 108°; when slowly heated above the m. p., the ester resolidifies, and then has m. p. 121°. It has b. p. 200°/12 mm. The 1 : 4- and the 2 : 4-dimethyl esters are both syrups, and the solution of the ammonium salt of the former gives a precipitate with concentrated solutions of copper sulphate, whilst that of the latter is precipitated even in dilute solution. The trimethyl ester has b. p. 194°/12 mm. (corr.), and solidifies in a freezing mixture at − 13° to a vitreous mass.

The 1-*amide*, $NH_2{\cdot}CO{\cdot}C_6H_3(CO_2H)_2$, is obtained by heating the corresponding ester with a concentrated solution of ammonia in methyl alcohol at 100° for one and a-half hours, then acidifying, removing trimellic acid by extracting with ether, and extracting several times with amyl alcohol. After removal of the amyl alcohol and recrystallising the residue from a mixture of methyl alcohol and benzene, the amide is obtained pure, and has m. p. 185—186°. The isomeric 2-*amide*, obtained by a similar method, has m. p. 199—200°. The 1-amide reacts with bromine and alkali, yielding 4-amino-*iso*phthalic acid, which was isolated in the form of its methyl ester (m. p. 130°). The 2-amide under similar conditions yields aminoterephthalic acid, which was isolated as its methyl ester, m. p. 123—126° (Cahn-Speyer, Abstr., 1907, i, 849, gives m. p. 133°). By the action of a methyl-alcoholic solution of ammonia on the anhydro-acid, a mixture of the 1- and 2-amides is obtained. J. J. S.

Ring Synthesis of Pyromellitic Acid. FRANZ FEIST (*Ber.*, 1911, **44**, 135—138).—Small amounts of pyromellitic acid (14% yield) are formed according to the equation: $2CO_2Et·CH_2·CHBr·CHBr·CO_2Et + 8KOH = C_6H_2(CO_2K)_4 + 4KBr + 4EtOH + 4H_2O + H_2$ when ethyl $\alpha\beta$-dibromoglutarate is mixed with alcoholic potassium hydroxide solution. The acid is isolated by acidifying the potassium salt and extracting eighteen times with ether. It is accompanied by large quantities of oily impurities, which can be removed by stirring with a small amount of ether in which the impurities dissolve. The anhydrous acid has m. p. 275°, and the tetramethyl ester, m. p. 141·5°.

J. J. S.

Preparation of Diglycollyldisalicylic Acid. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 227999).—*Diglycollyldisalicylic* [o-*diglycollyloxybenzoic*] *acid*, $O(CH_2·CO·O·C_6H_4·CO_2H)_2$, glistening leaflets, m. p. 168—170°, is readily prepared by boiling salicylic acid (or a salicylate) in benzene solution with diglycollic anhydride in the presence of an indifferent base (such as pyridine); it is of therapeutic importance, and compares favourably with acetylsalicylic acid in this respect.

F. M. G. M.

An *o*-Hydroxyaldehyde of Triphenylcarbinol. AUGUST BISTRZYCKI and MARTIN FELLMANN (*Ber.*, 1910, **43**, 3579—3586).—Salicylaldehyde can be condensed with benzylic acid, forming 4-hydroxy-3-aldehydotriphenylacetic acid (Abstr., 1910, i, 321), and this by the elimination of carbon dioxide is readily converted into 4-hydroxy-3-aldehydotriphenylcarbinol, which is the third aldehyde of the triphenylmethane series to be described.

4-Hydroxy-3-aldehydotriphenylacetic acid, prepared by the condensation of the components in benzene in presence of tin tetrachloride, crystallises, $+\frac{1}{2}C_7H_8$, in microscopic prisms or needles, m. p. 198—200° (from toluene), or in stellar aggregates of prisms, $+\frac{1}{2}C_6H_6$, m. p. 197—198° (from benzene).

The *azine*, $N_2[:CH·C_6H_3(OH)·CPh_2·CO_2H]_2$, derived from the action of hydrazine sulphate and sodium carbonate, is a yellow powder (decomp., 270—280°); the *sodium* salt crystallises in slender, yellow needles. The *oxime* crystallises in microscopic, colourless needles, which turn yellow at 110°, m. p. 226° (decomp.). The *semicarbazone* forms bunches of microscopic, slender, prismatic needles, m. p. 198—199° (decomp.). The *aniline* derivative is a granular, yellow powder, m. p. 85—86° (decomp.).

Methyl 4-methoxy-3-aldehydotriphenylacetate, prepared by the action of methyl sulphate in cold sodium hydroxide solution, crystallises in bunches of faintly yellow-coloured, four-sided prisms, m. p. 148—149°.

4-*Benzoxy-3-aldehydotriphenylacetic acid* crystallises in concentrically-grouped, colourless needles, m. p. 195·5—196·5°.

4-Hydroxy-3-aldehydotriphenylcarbinol (*loc. cit.*), prepared by the action of concentrated sulphuric acid on the aldehydo-acid, crystallises in aggregates of light yellow, prismatic plates, m. p. 123—124°, decomp. at 170°. The solution in concentrated sulphuric acid is

orange-red; a second isomeric form could not be obtained. The *acetyl* derivative crystallises in reniform aggregates of colourless prisms, m. p. 131—132°, the fused mass being orange-yellow. The *phenylhydrazone* forms rounded aggregates of microscopic prisms, decomp. 177°. The *oxime* separates in bunches of colourless, flat prisms; on heating, it becomes yellow and softens at 95°, becomes colourless, and solid again at 102°, m. p. 151° (decomp. 175°). The *semicarbazone* crystallises in colourless, microscopic needles, which become yellow at 140° and decompose at 164°, with an intense red coloration.

On heating the hydroxyaldehydocarbinol in a stream of dry air in a sulphuric acid bath at 190—200°, the anhydride, 2-*aldehydodiphenylquinomethane*, $CPh_2:C_6H_3O\cdot CHO$, is obtained as a brown powder. This darkens in colour at 100°, and begins to melt indefinitely at a somewhat higher temperature. E. F. A.

Hexahydroacetophenone [*cyclo*Hexyl Methyl Ketone] and Hexahydrobenzoylacetone. MARCEL GODCHOT (*Compt. rend.*, 1910, 151, 1131—1134).—Adipic acid is the sole product of the oxidation of *cyclo*hexyl methyl ketone by alkaline potassium permanganate. *cyclo*-Hexyl methyl ketone (Bouveault, Abstr., 1904, i, 61) forms an *oxime*, b. p. 145—150°/20 mm., m. p. 60°; no isomeric form was detected. It undergoes the Beckmann change, forming *acetylamino*cyclo*hexane* (*hexahydroacetanilide*), $C_6H_{11}\cdot NHAc$, crystallising in needles, m. p. 103°, identical with the product obtained by acetylating *cyclo*hexylamine.

Hexahydrobenzoylacetone, $C_6H_{11}\cdot CO\cdot CH_2\cdot COMe$, is obtained in the form of its *sodium* salt by the addition of sodium ethoxide to a mixture of *cyclo*hexyl methyl ketone and ethyl acetate. The diketone has b. p. 103—105°/25 mm., D^{15} 0·9933, and was prepared in the pure state from its *copper* derivative, which crystallises in pale green needles m. p. 210°; the phenylhydrazone and oxime appear to be oily.

W. O. W.

Ketones Derived from *o*-, *m*-, and *p*-Toluic Acids. JEAN B. SENDERENS (*Compt. rend.*, 1911, 152, 90—92. Compare Abstr., 1909, i, 286, 627; 1910, i, 11, 179, 489).—The under-mentioned ketones have been prepared by passing the vapour of an aromatic and an aliphatic acid over thorium oxide at 460—470°. A single distillation of the product usually suffices to yield the aromatic ketone in a state of purity. The new ketones are liquids; their odour resembles that of citrons in the case of the ortho-compounds, and of fennel in the case of the para-derivatives; the odour of the meta-compounds is not characteristic. The b. p.'s given are corrected.

o-Tolyl methyl ketone, b. p. 211°/745 mm., D_4^0 1·0262; *semicarbazone*, m. p. 192°. *m*-Tolyl methyl ketone, b. p. 221°/745 mm., D_4^0 1·0165; *semicarbazone*, m. p. 188° (decomp.). *p*-Tolyl methyl ketone, b. p. 224·5°/745 mm., D_4^0 1·0150; *semicarbazone*, m. p. 200°. *o*-Tolyl ethyl ketone, b. p. 224°/745 mm., D_4^0 1·0119; *semicarbazone*, m. p. 169°. *m*-Tolyl ethyl ketone, b. p. 234°/745 mm., D_4^0 1·0059; *semicarbazone*, m. p. 166°. *p*-Tolyl ethyl ketone, b. p. 238°/745 mm., D_4^0 1·0053; *semicarbazone*, m. p. 180°. *o*-*Tolyl propyl ketone*, b. p. 238·5°/758 mm.,

D_4^0 0·9936; *semicarbazone*, m. p. 176°. m-*Tolyl propyl ketone*, b. p. 247°/758 mm., D_4^0 0·9882; *semicarbazone*, m. p. 152°. p-*Tolyl propyl ketone*, b. p. 251·5°/758 mm., D_4^0 0·9774; *semicarbazone*, m. p. 190°. o-*Tolyl* iso*propyl ketone*, b. p. 230°/758 mm., D_4^0 0·9858; the *semicarbazone* is an oil. m-*Tolyl* iso*propyl ketone*, b. p. 238°/758 mm., D_4^0 0·9841; *semicarbazone*, m. p. 120°. p-Tolyl *iso*propyl ketone, b. p. 243°/758 mm., D_4^0 0·9778; *semicarbazone*, m. p. 101°. o-*Tolyl* iso*butyl ketone*, b. p. 247·5°/758 mm., D_4^0 0·9744; *semicarbazone*, m. p. 166°. m-*Tolyl* iso*butyl ketone*, b. p. 254°/758 mm., D_4^0 0·9712; *semicarbazone*, m. p. 172°. p-*Tolyl* iso*butyl ketone*, b. p. 259°/758 mm., D_4^0 0·9707; *semicarbazone*, m. p. 212°. W. O. W.

Quinones. HERMANN HAAKH (*J. pr. Chem.*, 1910, [ii], **82**, 546—551).—A theoretical paper in which an attempt is made to account for the recent numerous examples of the formation of highly-coloured additive compounds of *p*-benzoquinone with inorganic acids and salts, aromatic hydrocarbons, and other substances. The author assumes that the comparatively feebly-coloured *p*-benzoquinone itself has Graebe's peroxide constitution, in which the oxygen atoms have no residual affinity; when it forms highly-coloured additive compounds, the quinone acquires the Fittig constitution, addition occurring by means of the residual affinity of the oxygen atoms.

C. S.

Oxonium Hydrosulphides of *p*-Benzoquinone. M. M. RICHTER (*Ber.*, 1910, **43**, 3599—3603).—On mixing hydropersulphide and *p*-benzoquinone in anhydrous solvents at the ordinary temperature, a voluminous, brilliantly blue compound is obtained, which is labile in character and under certain conditions changes to a faintly yellow substance. The blue compound is obtained in presence of an excess of benzoquinone, the yellow with an excess of hydropersulphide.

The amorphous indigo-blue substance, *bis*-p-*benzoquinoneoxonium hydrotrisulphide*, $O{:}C_6H_4{:}O{<}^{H}_{S\cdot}{}^{}_{S\cdot}{}^{H}_{S}{>}O{:}C_6H_4{:}O$, decomposes at 115°, or when exposed to moisture. It dissolves in anhydrous solvents with an orange coloration, but is more or less decomposed.

By the action of *p*-benzoquinone dissolved in carbon disulphide and potassium hydrosulphide in absolute alcohol in a stream of hydrogen, p-*benzoquinoneoxonium hydrosulphide*, $O{:}C_6H_4{:}O{<}^{H}_{SK}$, is obtained as a dark greenish-black powder, extremely sensitive to traces of moisture.

Trisquinhydroneoxonium hydrosulphide, $C_{36}H_{32}O_{12}S$, is obtained by passing dry hydrogen sulphide through a solution of quinone in formic acid. It is a microcrystalline, almost black powder, decomp. 140°. The same compound is obtained on passing dry hydrogen sulphide over fused *p*-benzoquinone.

Hydropersulphide does not combine with substituted quinones; the entry of substituents, particularly of strongly negative groups, into the quinone molecule weakens the basic properties of oxygen and prevents salt formation. E. F. A.

Constitution of Quinhydrone-like Substances. M. M. Richter (*Ber.*, 1910, 43, 3603—3611).—The characteristics of oxonium salts, namely, simple addition of the components in their formation, ready decomposition in solution or when sublimed, and marked increase in the intensity of the colour, are also those of the quinhydrones. It is suggested that quinhydrones, phenoquinones, alloxantin, etc., are all to be regarded as oxonium compounds, and their dissociative and colour properties are due to quadrivalent oxygen and quinquevalent nitrogen. *p*-Benzoquinone has been shown (compare Siegmund, Abstr., 1909, i, 109; Meyer, *ibid.*, i, 395) to combine both with one and with two molecules of mono- and di-hydroxyphenols.

The evidence in favour of the formula $O\colon C_6H_4\colon O{<}^{H}_{O\cdot C_6H_4\cdot OH}$ for quinhydrone is discussed.

Two more must be added to the characteristics of the quinhydrones already enumerated, namely, they are composed of quinonoid and benzenoid sections, and they have the power of forming salts. The entry of substituting groups, particularly those of a strongly negative nature, into the quinone molecule materially lessens the basic properties of the oxygen atom, and in consequence prevents salt and quinhydrone formation.

Thirteen compounds are enumerated of six main types which are quinhydrone compounds of *p*-phenylenediamine, benzidine, and *p*-benzoquinonedichlorodi-imine.

It is considered that the simple oxygen atom generally behaves as a quadrivalent atom. E. F. A.

Preparation of *N*-Alkyl- and *N*-Arylaryl-sulphaminoanthraquinones. Fritz Ullmann (D.R.-P. 227324).—By the action of alkylsulphonamides of the general formula $R\cdot NH\cdot SO_2\cdot R_1$ (R = alkyl or aryl; R_1 = aryl) on halogenated anthraquinones, condensation products are obtained.

1-p-*Toluenesulphonylphenylaminoanthraquinone*,

$$C_6H_4{<}^{CO}_{CO}{>}C_6H_3\cdot NPh\cdot SO_2\cdot C_7H_7,$$

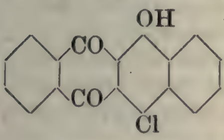
is prepared by heating together *p*-toluenesulphonylanilide and α-chloroanthraquinone in nitrobenzene solution in the presence of copper acetate and sodium carbonate; it crystallises from acetic acid in glistening, yellow crystals, m. p. 193°.

1-p-*Toluenesulphonylmethylaminoanthraquinone*, yellow needles, m. p. 192°, is prepared in a similar manner from *p*-toluenesulphonylmethylamide and α-chloroanthraquinone. By treatment with concentrated sulphuric acid, it yields α-methylaminoanthraquinone. F. M. G. M.

Preparation of 6-Chloro-1-hydroxynaphthacenequinone, and of 6-Chloro-1-hydroxynaphthacenequinone-4-sulphonic Acid. Anilinfarben and Extract-Fabriken vorm. J. R. Geigy (D.R.-P. 226230).—The work of Weizmann and others has shown that *o*-1-hydroxy-β-naphthoylbenzoic acid when heated with concentrated sulphuric acid and boric acid is converted quantitatively into 1-hydroxynaphthacenequinone (Trans., 1906, 90, 116; 1907, 91, 411;

1909, 93, 279); this reaction has now been extended to 4′-chloro-1′-hydroxy-β-naphthoyl-*o*-benzoic acid (Abstr., 1910, i, 746) and its sulphonic acids.

6-*Chloro*-1-*hydroxynaphthacenequinone* (annexed formula) was prepared by dissolving crystallised boric acid (6 parts) in 80 parts of concentrated sulphuric acid (25% SO_3), slowly adding the 4′-chloro-1′-hydroxy-β-naphthoylbenzoic acid (20 parts), and heating at 70° until sodium hydroxide ceased to produce a yellow coloration. The product after crystallisation from benzene formed long, reddish-yellow needles, m. p. 307°, and seems not to be identical with the 6-chloro-1-hydroxynaphthacenequinone, m. p. 290—293° (Trans., 1907, 91, 418). The *sodium* salt is insoluble in water.



6-*Chloro*-1-*hydroxynaphthacenequinone*-4-*sulphonic acid* was isolated in the form of its *monosodium* salt, a brick-red powder, by boiling with a saturated solution of sodium chloride; it is soluble in water with a yellow coloration; the *disodium* salt was obtained as a dark red gelatinous precipitate soluble in water with a blue coloration.

F. M. G. M.

Preparation of Alkyloxyacetyl Derivatives of Menthols. Alfred Einhorn (D.R.-P. 225821).—The interaction of ethoxyacetic acid and mentholcarboxyl chloride in a cooled ethereal solution yields *menthol ethoxyacetate*, a colourless oil, b. p. 144°/14 mm. The reaction is a general one for the alkyloxyacetic acids and mentholcarboxyl halides.

F. M. G. M.

Preparation of Santalyl Alkylaminoacetates. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 226229).—It is found that santalyl alkylaminoacetates of therapeutic importance can be prepared by treating chloroacetylsantalol with a secondary amine. *Chloroacetylsantalol*, a viscous, yellow oil, was prepared by treating santalol with chloroacetyl chloride in the presence of pyridine, or with chloroacetic acid, pyridine, and carbonyl chloride. This product was isolated, mixed with a solution of dimethylamine in benzene, and left during twenty-four hours; the *santalyl dimethylaminoacetate* was extracted with hydrochloric acid, and, on rendering the solution alkaline with sodium carbonate, separated as a yellow, odourless oil, which hydrolyses readily with alkalis into its components. It forms well characterised salts; the *hydrochloride* crystallises from acetone in odourless, colourless needles, m. p. 154°. Analogous compounds can be prepared with diethylamine or piperidine.

F. M. G. M.

Catalytic Reactions at High Temperatures and Pressures. XXII. Reduction of Terpenes. Wladimir Ipatieff (*Ber.*, 1910, 43, 3546—3553. Compare Sabatier and Senderens, Abstr., 1901, i, 459; Vavon, Abstr., 1910, i, 52, 400).—By reducing *l*-limonene with hydrogen at 280—300° under 110—120 atmospheres' pressure, using cupric oxide as the catalyst, an unsaturated hydrocarbon, $C_{10}H_{18}$, b. p. varying from 172° to 176°, is obtained. The same hydrocarbon is also

produced when copper is used, but a higher temperature is necessary. Further reduction of this hydrocarbon leads to the formation of *p*-menthane.

[With DRACHUSSOFF.]—French *l*-pinene in the presence of iron is not reduced, but undergoes isomerisation to dipentene. At 265° with cupric oxide as catalyst, it is reduced to a hydrocarbon, $C_{10}H_{18}$, whilst repeated reduction at 280—290° yields a hydrocarbon, $C_{10}H_{20}$, b. p. 163—170°, D^{20} 0·7949. Similar results were also obtained with metallic copper. With nickel oxide, the reduction takes place with great rapidity and at a lower temperature than with cupric oxide, $C_{10}H_{20}$ being formed.

It is considered probable that the hydrocarbon, $C_{10}H_{20}$, obtained from *l*-pinene consists of a mixture of *o*- and *p*-menthanes.

For the purpose of comparison, menthane was prepared from cymene by reducing with hydrogen, nickel oxide being used as a catalyst; it had b. p. 167—170°, D^{20} 0·8038. F. B.

Peppermint Oil Prepared from Dry Leaves of Mentha piperita. J. MURAOUR (*Bull. Soc. chim.*, 1911, [iv], **9**, 66—67).—Dry leaves, which had fallen naturally from mint plants during cultivation, gave a yield of from 400 to 500 grams of oil per 100 kilos. of leaves. This oil was yellow, and had an odour recalling that of Japanese peppermint oil. Two samples gave the following constants: D^{15} 0·911 to 0·913, $a_D = -38°18'$ to $-40°4'$, solubility 1 in 1·5 to 2·5 vols. of alcohol at 80°, and contained 33·16 to 40·31% of esters and 43·99 to 45·67% of total menthol. The results of examination of commercial peppermint oils indicated that some of these products consisted of true peppermint oil of French origin mixed with oil from the fallen leaves.

T. A. H.

Essential Oils. I. Orange Flower Oil. II. Schinus molle Oil. G. LALOUE (*Bull. Soc. chim.*, 1910, [iv], **7**, 1101—1107, 1107—1109).—A more detailed account of work already published (Abstr., 1910, i, 755; 1909, i, 817). Gildemeister and Stephan's observation (Abstr., 1897, i, 81) that *Schinus molle* oil contains pinene and phellandrene is confirmed, and there is probably also about 20% of sesquiterpenes present. Oil distilled from branches and leaves, obtained at Grasse, was richer in pinene than oil from leaves and branches obtained in Algeria. T. A. H.

Milk Sap of Antiaris toxicaria. HEINRICH KILIANI (*Ber.*, 1910, **43**, 3574—3579. Compare Abstr., 1897, i, 91).—Seligmann (Abstr., 1903, ii, 314) obtained from the juice of *A. toxicaria* procured from Sarawak an antiarin differing from that previously described. It is now found with juice obtained from Java that two antiarins exist, the new *β*-form being present in the larger proportion. They differ in crystalline form, melting point, water of hydration, and composition, although there is no difference in their toxic character.

α-Antiarin, $C_{27}H_{42}O_{10},4H_2O$, crystallises in glistening plates or leaflets, m. p. 220—225°.

β-Antiarin, $C_{27}H_{38}O_{10},3H_2O$ or $C_{28}H_{38}O_{10},3H_2O$, crystallises in slender needles or bunches of columnar needles, m. p. 206—207°.

Emulsin is without action on either glucoside; the products of hydrolysis of β-antiarin have not been characterised. E. F. A.

Digitonin, Digitogenic Acid and their Oxidation Products. HEINRICH KILIANI (*Ber.*, 1910 **43**, 3562—3574. Compare Abstr., 1904, i, 505).—A further study of the oxidation products of digitogenin shows that digitic acid has the composition $C_{28}H_{42}O_{11}$. Molecular weight determinations are particularly difficult to carry out in the case of oxidation products of digitogenic acid. It has not been found possible so to conduct oxidation as to obtain simple products of known constitution; even with ozone, the chief product is an acid, $C_{26}H_{40}O_7$.

To prepare digitonin, German digitalis is extracted with alcohol ether, the insoluble residue is dissolved in water, the vessel placed in a bath of water at 70°, a small quantity of amyl alcohol added, and, after inoculation, the whole is allowed to cool slowly until crystallisation is complete.

Digitic acid is tribasic, the barium salt being $(C_{28}H_{41}O_{12})_2Ba_3,18H_2O$. The normal potassium salt is hygroscopic, and the acid salt admixed with free acid; the calcium salt is amorphous, so that neither is suitable for analysis. The by-products of the oxidation consisted of acids miscible with sodium chloride solution, from which no chemical individual could be isolated, and of acids insoluble in salt solution. When further oxidised with permanganate in strongly alkaline solution, a definitely crystalline calcium salt, $C_{19}H_{26}O_7Ca,8H_2O$, was obtained (compare Kiliani and Baylen, Abstr., 1895, i, 65). The acid is indefinitely crystalline, m. p. 170° (decomp.).

Anhydrodigitic acid, when oxidised with potassium permanganate in neutral solution, forms an acid, $C_{26}H_{38}O_7$, crystallising in crusts of small pyramids, m. p. 196—200°; the magnesium salt crystallises in needles and small pyramids.

From the products of oxidation of digitogenic acid by hot permanganate in neutral solution, a new tribasic *acid*, $C_{28}H_{42}O_{11}$, has been isolated; it crystallises in leaflets, m. p. 155° (decomp.). The *barium* salt, $C_{28}H_{40}O_{11}Ba,10H_2O$, crystallises in aggregates of closely-packed needles and is strongly acid. The acid is isomeric with digitic acid.

On oxidation of digitogenic acid with ozone, more than 60% of an *acid*, $C_{26}H_{40}O_7$, is obtained; this crystallises in clusters of pyramids, m. p. 222°. A *magnesium* salt, $C_{26}H_{38}O_7Mg,11H_2O$, crystallises also in tiny pyramids. It has not been established in what form the two atoms of carbon are eliminated during the oxidation. E. F. A.

Saponification of Sinigrin. MAX GONNERMANN (*Pflüger's Archiv*, 1911, **137**, 453—469).—Sinigrin is not acted on by any enzyme with the exception of myrosin. The enzymes investigated under varying conditions of solvent, etc., were of both animal and vegetable origin; bacteria, including those in the intestine, have no effect in liberating allylthiocarbimide. This confirms Kobert's statement. Various details regarding the mode of preparation of this glucoside are given.

W. D. H.

A Saponin-Cholesterol Compound. S. Yagi (*Arch. exp. Path. Pharm.*, 1910, **64**, 141—146).—Ransom having shown that cholesterol inhibits the hæmolytic power of saponin, Windaus found that certain saponins form additive products with cholesterol; the digitonin-cholesterol compound, for instance, is crystallisable, and has the formula $C_{82}H_{140}O_{29}$, that is, a combination of one molecule of each substance ($C_{55}H_{94}O_{28}+C_{27}H_{46}O$). Other cholesterides have been separated by the same author. The present paper gives details of the preparation and properties of another crystallisable cholesteride, namely, that of dioscine, in which three molecules unite with two of cholesterol, $3C_{24}H_{38}O_6,2C_{27}H_{46}O,1$ or $2H_2O$, a microcrystalline powder, m. p. 223°; this is inactive on blood corpuscles. The feeble hæmolytics, such as Merck's saponin, sapotoxin, and dioscorea-sapotoxin, need about an equimolecular amount of cholesterol to render them inactive; half the amount leaves them still partly active; the feeble members of the group therefore do not contain active mixed with inactive molecules.

W. D. H.

Action of Nitric Acid on Aloins; Production of Tetranitroaloe-emodin and of 2 : 4 : 6-Trinitro-3-hydroxybenzoic Acid. Eugène Léger (*Compt. rend.*, 1910, **151**, 1128—1131; *Bull. Soc. chim.*, 1911, **9**, 88—97).—It has long been known that chrysammic acid and picric acid are amongst the products of the action of nitric acid on the aloins. It is now shown that the production of these compounds is preceded by the formation of two other substances, which are then converted into these acids by the further action of nitric acid.

Tetranitroaloe-emodin, $C_{15}H_6O_5(NO_2)_4$, arises from the action of nitric acid (D 1·2) on barbaloin or *iso*barbaloin at the temperature of the water-bath. It occurs in slender, golden needles, m. p. about 285° with deflagration. On long boiling with nitric acid (D 1·32), it is converted into chrysammic acid.

The mother liquor from the tetranitroaloe-emodin contains 2 : 4 : 6-trinitro-3-hydroxybenzoic acid (Griess, *Annalen*, 1861, **117**, 28); this crystallises from ether in almost colourless, efflorescent, rhombic lamellæ, m. p. 185·5—186·5° (corr.). It loses carbon dioxide when heated with nitric acid, and forms picric acid.

Tetranitrorhein, $C_{14}HO_2(NO_2)_4(OH)_2 \cdot CO_2H$, is probably an intermediate product in the conversion of tetranitroaloe-emodin into chrysammic acid. It has been isolated as short, efflorescent prisms.

W. O. W.

Chlorophyll. X. Comparative Investigation of Chlorophyll from Different Plants. II. Richard Willstätter and Alfred Oppé (*Annalen*, 1910, **378**, 1—18. Compare Willstätter, Hocheder, and Hug, Abstr., 1910, ii, 150).—An examination of the leaves of 200 species of plants has shown that the chlorophyll present is the so-called amorphous or wax-like form which yields phytol. The phæophytin obtained from the dried leaves gives a 33% yield of phytol, provided the extraction is carried out rapidly. In

many cases, for example, grass and plantains, good yields of phytol are also obtained when a slow method of extraction is used, but in others the amount of phytol isolated diminishes as length of time taken for the extraction is increased. Thus the yields of phytol from *Heracleum spondylium* are 6·0 when the extraction takes twenty-four hours, 20·2 for one hour, and 31·5% for three-quarters of an hour.

It is evident that the chlorophyll loses its phytol when its alcoholic solution is left in contact with the plant tissues, and this loss is due to enzyme action (Willstätter and Stoll, next abstract). The results account for the low percentages of phytol obtained in previous experiments (*loc. cit.*), as the slow method of extraction was used. The increase observed in the amount of phytol when the dried material is kept can be accounted for by the enzyme losing its activity with age.

Two quick methods of extraction are described. The one consists in rubbing the leaf powder with chalk and sufficient alcohol to form a thick paste (about 1 litre per kilo. of leaf powder), leaving for five minutes, filtering under pressure, and washing with small amounts of alcohol. The second method consists in making a much stiffer paste, 300 c.c. of alcohol for 1 kilo. of powder, and placing on a percolator and using low pressures. This second method is the better when comparatively concentrated solutions of chlorophyll are required.

The phæophytin was obtained by the addition of oxalic acid to the extract. When chlorophyll had not undergone decomposition, a fine compact precipitate of phæophytin mixed with oxalates was obtained, but if much phytol has been formed, the precipitate had a voluminous, coagulated appearance.

Phytochlorin-*e* and phytorhodin-*g* have been isolated from the phæophytin from 125 different plant species. The amount of phytorhodin-*g* diminishes as the boiling with the alcoholic potassium hydroxide is increased, or as the concentration of the alkali is increased. In many cases a phytochlorin somewhat more feebly-basic than phytochlorin-*e* was isolated. The usual method of hydrolysis was boiling for two to three hours with 24% methyl-alcoholic potassium hydroxide, using 5 c.c. of solution for 1 gram of phæophytin. J. J. S.

Chlorophyll. XI. Chlorophyllase. RICHARD WILLSTÄTTER and ARTHUR STOLL (*Annalen*, 1910, **378**, 18—72).—Willstätter and Oppé (preceding abstract) have shown that the conversion of amorphous chlorophyll into crystallised chlorophyll is accompanied by the elimination of a phytol group, and that the change occurs when the process of extraction is slow, but can be avoided by using a rapid method of extraction. It is now shown that crystallised chlorophyll contains one methoxy- and one ethoxy-group and not two methoxy-groups (Willstätter, Hocheder, and Hug, Abstr., 1910, ii, 150), and that the amorphous chlorophyll contains one methoxy- and one phytyl group; it is proved that the change of the amorphous into the crystallised chlorophyll is a process of alcoholysis, and in each stage of the change the phytol eliminated is equivalent to the ethyl alcohol

entering the molecule. The reaction, which is represented by the equation:

$$CO_2H\cdot C_{31}H_{29}N_4Mg(CO_2Me)\cdot CO_2\cdot C_{20}H_{39} + EtOH = C_{20}H_{39}\cdot OH + CO_2H\cdot C_{31}H_{29}N_4Mg(CO_2Me)\cdot CO_2Et,$$

takes place in the presence of a specific enzyme, *chlorophyllase*, which belongs to the group of esterases. Other substances of the same group, for example, lipase from linseed or pancreas lipase, cannot bring about the same change. The enzyme reacts slowly with phæophytin, and does not react at all with waxes of an ester nature. It is highly probable that the enzyme brings about the formation of phytyl esters in the plant. Working with methyl alcohol, it has been found possible to replace the phytoxyl groups by methoxyl (methanolysis) and in the presence of moist ether to replace the phytoxyl group by hydroxyl (hydrolysis). Lipases, on the other hand, produce hydrolysis, but do not appear able to induce alcoholysis.

The following system of nomenclature is suggested for chlorophyll derivatives: the tricarboxylic acid, $C_{31}H_{29}N_4Mg(CO_2H)_3$, from which chlorophyll is derived is called *chlorophyllin*; the monomethyl ester obtained by the hydrolysis of chlorophyll is termed *chlorophyllide*; amorphous chlorophyll is *phytylchlorophyllide*; Borodin's crystallised chlorophyll is *ethylchlorophyllide*; the magnesium-free compound,

$$C_{31}H_{31}N_4(CO_2H)_3,$$

is termed *phaeophorbide*; phæophytin is thus *phytylphaeophorbide*, and the compound hitherto called phæophorbin is *ethylphaeophorbide*.

A rapid method for the extraction of chlorophyll is described which differs somewhat from those recommended by Willstätter and Oppé (preceding abstract). It consists in moistening 1 kilo. of the leaf meal for five minutes with 0·5 litre of alcohol (96%), then spreading on a thimble, and applying suction for a short time. The addition of alcohol, and suction, are used alternately until a further litre of alcohol has been added; in the course of twenty minutes, 1 litre of solution is obtained; by washing with alcohol, a further 0·9 litre of extract is obtained in thirty-five minutes more. The amount of chlorophyll in the two extracts is 80% of the total present. The solutions, although dilute, are purer than those obtained by the methods already described, and therefore yield more phæophytin.

For the estimations of phytol the method already described (Abstr., 1910, ii, 150) has been used. The amount of chlorophyll transformed into ethylchlorophyllide by means of chlorophyllase has been determined both by the estimation of the phytol liberated and by determining the amount of silver iodide obtained from the product by Zeisel's method. Details for the calculations are given. The results obtained by the two methods agree, indicating that the ethyl groups entering the molecule are equivalent to phytyl groups removed. It is highly probable that the reaction is a direct exchange of alkyl for phytyl groups, and that it does not consist in the hydrolysis of the phytyl ester to the acid and the subsequent conversion of this into the ethyl ester. The enzyme was in the form of leaf meal from which the chlorophyll had been extracted, and was used whilst moist with alcohol. The reaction was most rapid when the mixture was kept well shaken, and in each experiment the flasks were well corked in order to prevent

the admission of moisture. Although the reaction mixture is non-homogeneous, it is probable that the diffusion phenomena are such that the mixture behaves as if it were a homogeneous one. The values of K, however, when calculated by means of the equation for a unimolecular reaction, are not constant, but diminish as t increases. This is shown to be due partly to the fact that the enzyme tends to become less active when kept for some time. With varying amounts of enzyme, Schütz's rule, $\mu = K\sqrt{E.t}$, holds good approximately. With chlorophyll solutions of different concentrations, the amount transformed in a given time is roughly proportional to the concentration. The addition of water to the alcoholic solutions accelerates the activity of the chlorophyllase; thus the value of $K \times 10^3$ after ten hours varies from 28 to 37 using 92% alcohol, but with 80% alcohol $K \times 10^{13}$ has the values 175, 166, and 80. Even in 80% alcohol the reaction is a true alcoholysis and not hydrolysis. The activity of the enzyme is less at 35° than at 25°; when boiled with alcohol the enzyme is gradually destroyed, and in drying leaves for the preparation of the enzyme it is necessary to avoid high temperatures. Calcium carbonate has no effect on the alcoholysis, whereas magnesium hydroxide has an appreciable retarding effect. Young leaves appear to contain a smaller amount of enzyme than older ones, and the amount tends to increase as the chlorophyll increases.

The methylchlorophyllide, obtained by using methyl in place of ethyl alcohol, is formed much less readily, and its isolation is rendered difficult by the readiness with which it is transformed into readily soluble derivatives. The reaction proceeds more readily in the presence of a small amount of water, for example, in 92% methyl alcohol, but the best results are obtained by treating fresh leaves with 50—60% methyl alcohol. The product varies with the species of plant used; that obtained from *Heracleum*, $C_{72}H_{70}O_{11}N_8Mg_2$, crystallises from ether, in which it is sparingly soluble, in steel-blue, glistening prisms. The corresponding *methylphaeophorbide*, $C_{72}H_{74}O_{11}N_8$, forms glistening, spindle-shaped crystals with a metallic lustre. The methylchlorophyllide from stinging nettles is somewhat more readily soluble in ether, and crystallises in triangular and hexagonal plates.

Chlorophyllide, $CO_2Me{\cdot}C_{31}H_{29}N_4Mg(CO_2H)_2$, may be obtained by the action of the enzyme on a moist ethereal solution of chlorophyll in the absence of alcohol. It forms green plates and is extremely unstable, and is transformed readily into the isomeric *magnesium phaeophorbide*, $CO_2Me{\cdot}C_{31}H_{31}(CO_2)_2Mg$, which forms black crystals readily decomposed by acid.

The synthesis of chlorophyll from chlorophyllide and phytol can be accomplished by means of chlorophyllase, but the yields are small. Chlorophyll always appears to be accompanied by chlorophyllase; in *Sorbus aucuparia*, *Mellitis melissoph.*, *Stachys silvitica*, *Lamium maculatum*, and *Heracleum* the amount of enzyme is comparatively large. The presence of the enzyme in stinging nettles, grass, *Sambucus*, *Aspidium*, *Equisetum*, *Taxus*, *Avena*, and *Platanus* can be demonstrated by the prolonged action of the tissue on the chlorophyll extract, when products are obtained which contain but little combined phytol.

Extracts of stinging nettles and of *Platanus* react with the enzyme

from *Galeopsis* or *Heracleum* more readily than with their own enzymes, but the alcoholysis does not proceed to completion. Under conditions which result in the complete alcoholysis of the chlorophyll of *Galeopsis* or *Heracleum*, only 66% of the chlorophyll of stinging nettles is decomposed. The chlorophyll of *Heracleum* reacts only slowly with stinging-nettle meal, but the rate is greater than that between stinging-nettle meal and the chlorophyll from stinging-nettle extract. J. J. S.

Chlorophyll. XII. Phytol I. Richard Willstätter, Erwin W. Mayer, and Ernst Hüni (*Annalen*, 1910, **378**, 73—152. Compare Willstätter and Hocheder (Abstr., 1907, i, 784).—Crude phytol and the distilled product are not identical but isomeric, and the process of distillation appears to produce a shifting of a double linking. The two are termed respectfully α- and β-phytol. An examination of the products of oxidation shows that the α-compound has the olefine linking between carbons 5 and 6, as it yields a ketone, $C_{15}H_{30}O$, whereas β-phytol yields a ketone, $C_{13}H_{26}O$, and contains an olefine linking between carbons 7 and 8. The chief oxidation products isolated are the following ketones and acids. (1) Ketone, $C_{15}H_{30}O$, obtained from α-phytol by means of chromic anhydride, or from the α-ozonide. (2) Ketone, $C_{13}H_{26}O$, from β-phytol by means of chromic anhydride, from the β-ozonide, or from the acid $C_{14}H_{28}O_2$ by means of chromic acid. (3) Ketone, $C_{11}H_{22}O$, from trihydroxyphytan and chromic acid, or by the action of ozone on the ketones 1 and 2. (4) Ketone, $C_9H_{18}O$, by the action of ozone on any of the other ketones. (5) Acid, $C_{14}H_{28}O_2$, from α-phytol and ozone, from trihydroxyphytan and chromic acid, or from the ozonide of the olefine $C_{15}H_{30}$. (6) Acid, $C_{12}H_{24}O_2$, from the ketone, $C_{15}H_{30}O$ and ozone, from the ketone $C_{13}H_{26}O$ and chromic acid, or from the acid $C_{14}H_{28}O_2$ and chromic acid. (7) Acid, $C_{10}H_{20}O_2$, from the ketone $C_{15}H_{30}O$ and ozone, and from the ozonide of the olefine $C_{15}H_{30}$.

The first two ketones are easily obtained in a state of purity, but the two lower ones are more difficult to prepare. They are all methyl ketones, although they yield only traces of bromoform with hypobromite and only small amounts of methylamine by the Beckmann transformation. The presence of the acetyl group in the ketone $C_{15}H_{30}O$ can be demonstrated by the following series of reactions: $C_{13}H_{27}\cdot CO\cdot CH_3 \longrightarrow C_{13}H_{27}\cdot CH(OH)\cdot CH_3 \longrightarrow C_{13}H_{27}\cdot CH{:}CH_2 \longrightarrow C_{13}H_{27}\cdot CH(OH)\cdot CH_2\cdot OH \longrightarrow C_{13}H_{27}\cdot CO_2H$. The four ketones resemble one another in physical properties. They are pale yellowish-green oils with relatively high b. p.'s, and it is suggested that the compounds, especially the lower members, have the tautomeric enolic structure. The acids are saturated and do not decolorise bromine, but react readily with permanganate. They do not crystallise, and resemble phytol in physical properties.

The reduction products of phytol and also numerous esters have been prepared.

α-Phytol contains the double linking in the βδ-position with respect to the $CH_2\cdot OH$-group, as the phytenic acid obtained by oxidising with chromic acid is an αβ-unsaturated acid, and the following structural

formula is suggested: $CHMe_2\cdot[CHMe]_5\cdot CMe\colon CMe\cdot CHMe\cdot CH_2\cdot OH$. It is possible that α-phytol is a condensation product of isoprene,

$$4C_5H_8 + H_2O + 3H_2 = C_{20}H_{40}O.$$

The formula suggested for β-phytol is

$$CHMe_2\cdot[CHMe]_4\cdot CMe\colon CMe\cdot[CHMe]_2\cdot CH_2\cdot OH.$$

α-Phytol has D_4^{20} 0·856 and n_D^{20} 1·46364, and β-phytol, D_4^{20} 0·852 and n_D^{20} 1·46380. It can be distilled in portions of 10—30 grams from Claisen flasks, and has b. p. 203—204°/9—10 mm. Both compounds give the same iodine number. A good test for the presence of phytol, for example, in phæophytin preparations, is the formation of a stable, colourless oil by heating for a short time with concentrated nitric acid. When the boiling is prolonged, a nitrogenous acid is formed, the alkaline solutions of which have an intense yellow colour. Many phytol preparations, both crude and distilled, undergo autoxidation (Engler and Weissberg, Abstr., 1899, i, 189) when kept for several months in corked vessels. A sharp, penetrating odour with an acid reaction is noticeable, and the oil becomes limpid and, at the same time, distinctly acid. The formation of a peroxide can be detected by Engler's method. The rate of autoxidation varies considerably with different samples, and it is probable that small amounts of some impurity, present in both the crude and the distilled products, act as a catalyst. The acid formed is not homogeneous and is unsaturated; the analytical numbers indicate that it may be a mixture of equal amounts of phytenic acid and a saturated acid with 10 carbon atoms.

Phytyl hydrogen phthalates, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{20}H_{39}$, are formed when the phytol and phthalic anhydride are boiled for five hours with benzene, and can be isolated by making use of the fact that their sodium salts are very sparingly soluble in water, but are soluble in ether. The α-phytyl ester is a syrup, readily soluble in most organic solvents; it yields an oily *dibromide*, which is unstable, and a *silver* salt, $C_{28}H_{43}O_4Ag$, in the form of minute, flat prisms, m. p. 119°; the isomeric *silver β-phytyl phthalate* crystallises in prisms, m. p. 116°.

Cetyl hydrogen phthalate, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{16}H_{33}$, forms indefinite crystals of a waxy consistency, and has m. p. 61—62°. The *silver* salt, $C_{24}H_{37}O_4Ag$, crystallises from benzene.

Phytyl ether, $O(C_{20}H_{39})_2$, obtained by the action of concentrated sulphuric acid on a glacial acetic acid solution of the alcohol, is a viscid oil sparingly souluble in glacial acetic acid or in methyl alcohol, and forms a dibromide.

Phytol cannot be reduced by means of sodium and ethyl or amyl alcohol, but by electrolytic reduction in cold alcoholic sulphuric acid solution, using platinised platinum electrodes with a voltage of 6 and a current density of 3 ampere per sq. m. and an earthenware diaphragm, the saturated alcohol, *phytanol* (*dihydrophytol*), $C_{20}H_{42}O$, is obtained together with the hydrocarbon phytan. Phytanol is readily prepared by reducing phytol with hydrogen in ethereal solution, using platinum-black as catalyst; a slow stream of hydrogen is passed through for about three weeks when 40 grams of phytol are used. The reduction is much quicker when the hydrogen is used under slight pressure and the apparatus is shaken continuously. It is a colourless, odourless oil, has b. p. 201·5—202°/9·5 mm., is miscible with all organic

solvents, and is isomeric with arachyl alcohol (Haller, Abstr., 1907, i, 377). It forms a *sodium* derivative, $C_{20}H_{41}\cdot ONa$, in the form of a viscid oil, soluble in ether or light petroleum.

The *phenylurethane*, $NHPh\cdot CO\cdot O\cdot C_{20}H_{41}$, obtained by the combination of the alcohol with phenylcarbimide, is also a thick oil. *Phytanyl hydrogen phthalate*, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{20}H_{41}$, is a syrup, and its *silver* salt, $C_{28}H_{45}O_4Ag$, has m. p. 106—106·5°. *Phytanyl pyruvate*,

$$CH_3\cdot CO\cdot CO_2\cdot C_{20}H_{41},$$

obtained by heating the components at 110—120°, or more readily by shaking the alcohol for a long time at the ordinary temperature with five times its weight of pyruvic acid and removing the excess of acid by means of water, has b. p. 219—220°/10 mm.; its *semicarbazone*, $C_{23}H_{47}O_3N_3$, crystallises from methyl alcohol in needles, m. p. 88—91°. *Cetyl pyruvate* has m. p. 26·5—27·5°, and its *semicarbazone*, $C_{19}H_{39}O_3N_3$, crystallises in flat prisms, m. p. 140—141°.

The esterification of β-phytol by means of glacial acetic acid at 155° has been studied; at the end of one hour, 34·5% of the acid is transformed into ester, but after one hundred and forty-four hours the yield has fallen to 6·9%, owing to decomposition of the ester into phytadiene. Geraniol and nerol react in much the same manner with glacial acetic acid at 155°. The initial rates of esterification with acetic acid at 155° of the following unsaturated alcohols have been determined: oleyl alcohol, erucyl alcohol, geraniol, nerol, cholesterol, and the values obtained are smaller than those for the corresponding saturated alcohols. *Erucyl alcohol*, $C_{22}H_{44}O$, prepared by reducing ethyl erucate with boiling amyl alcohol and sodium, has b. p. 240·5—241·5°/10 mm., and forms rhombohedral crystals, m. p. 34·5—35·5°. Its *dibromide*, $C_{22}H_{44}OBr_2$, forms glistening prisms, m. p. 45—45·5°. When reduced with hydrogen in the presence of finely-divided platinum, the unsaturated alcohol yields *docosyl alcohol*, $C_{22}H_{46}O$, which crystallises from chloroform in glistening prisms, m. p. 71—71·5°; the *phenylurethane*, $C_{29}H_{51}O_2N$, crystallises from ethyl acetate in glistening prisms, m. p. 86—86·5°. The percentages of acetic acid transformed into ester at 155° are the following: dihydrophytol, 73; arachyl alcohol, 76·2; tetrahydrogeraniol, 68·5. These values are lower than those given by normal alcohols.

Phytanic acid, $C_{20}H_{40}O_2$, is best prepared by oxidising dihydrophytol with an acetic acid solution of chromic acid in the presence of potassium hydrogen sulphate, and forms a viscid oil, b. p. 221°/7·5 mm. The *silver* salt, $C_{20}H_{39}O_2Ag$, darkens at 165° and has m. p. 177—177·5°. The *amide*, $C_{19}H_{39}\cdot CO\cdot NH_2$, crystallises when its solutions in methyl alcohol or light petroleum are well cooled, and has m. p. 53—53·5°. Δ^{β}-*Phytenic acid*, $C_{20}H_{38}O_2$, is formed together with the ketone, $C_{15}H_{30}O$, when phytol is oxidised with an acetic acid solution of chromic anhydride (5 atoms of O) in the presence of potassium hydrogen sulphate. It forms a yellow oil, b. p. 210—220°/11·5 mm., and has D_4^{20} 0·917 and n_D^{20} 0·893. The position of the ethylene linking is established by the readiness with which it yields a γ-lactone (Abstr., 1907, i, 786) when heated with sulphuric acid and water. The saturated hydrocarbon, *phytane*, $C_{20}H_{42}$, is most readily obtained by reducing phytene with hydrogen and platinum; it is a colourless,

mobile oil, with b. p. 169·5°/9·5 mm. and D_4^{20} 0·803, is only sparingly soluble in cold methyl alcohol, and solidifies when cooled by liquid air. In the preparation of phytene (Abstr., 1907, i, 786) a *di-iodo-derivative*, $C_{20}H_{40}I_2$, is obtained in the form of a heavy oil, and when this is reduced with zinc dust and glacial acetic acid, or with zinc dust and hydriodic acid, it yields impure phytene, although the two iodine atoms are not attached to adjacent carbon atoms. *Phytadiene*, $C_{20}H_{38}$, is formed when β-phytol, phthalic anhydride, and benzene are heated for a day in a Babo funnel, owing to the readiness with which the phytyl hydrogen phthalate decomposes into phytadiene and phthalic acid; it has b. p. 186—187°/13 mm. and D_4^{20} 0·826, and its iodine number points to the presence of two olefine linkings.

α-Phytol ozonide, prepared by passing a current of 6% ozone into a dry chloroform solution of the alcohol and then removing the chloroform under reduced pressure at 20°, forms a pale green syrup with a pungent odour, and dissolves readily in most organic solvents. Methyl alcohol separates the crude ozonide into an insoluble "moloxide," $C_{20}H_{40}O,O_2$, and a soluble oxozonide, $C_{20}H_{40}O,O_4$. The yield of the "*moloxide*" is larger the shorter the time of ozonising, and it canbe obtained crystalline by well cooling its methyl alcoholic solution. It is an oil at the ordinary temperature, and when boiled with water yields the same products and in the same amounts as the oxozonide. This latter, when kept for some months under reduced pressure over phosphoric anhydride, yields the normal *ozonide*, $C_{20}H_{40}O,O_3$.

The best yields of the ketone, $C_{15}H_{30}O$, are obtained when α-phytol is oxidised with a glacial acetic acid solution of chromic anhydride in the presence of potassium hydrogen sulphate. With the theoretical amount of oxygen, only a small amount of the alcohol is oxidised; but with 4 to 5 atoms of oxygen to each molecule of alcohol, a 73—97% yield of ketone can be obtained. The same ketone is also formed when either of the ozonides of α-phytol is boiled with water for three hours in a reflux apparatus, using 25 grams at a time. The aqueous solution has a decided acid reaction, and gives the ordinary reactions for aldehydes. The oily product consists of the ketone together with the acid $C_{14}H_{28}O_2$ (3·5%), phytenic acid, the hydrocarbon $C_{15}H_{32}$, and a small amount of an ether. The acids can be removed by extraction with very dilute sodium hydroxide solution, and the ketone purified by distillation under reduced pressure. It forms a pale yellowish-green, limpid oil, which turns quite colourless in the course of two to three weeks. It has b. p. 173—174°/9 mm. and 291·8—292·4°/722 mm., and is optically inactive. The *oxime*, $C_{15}H_{31}ON$, is a viscid oil with b. p. 201—202°/10 mm. and D_4^0 0·885; the *semicarbazone*, $C_{16}H_{33}ON_3$, crystallises from alcohol in well-developed prisms, m. p. 64·5°, and the p-*nitrophenylhydrazone*, $C_{21}H_{35}O_2N_3$, forms a pale yellow oil. The ketone combines with bromine in chloroform solution, yielding an unstable dibromide, which is probably derived from the isomeric enolic compound. Many ketones, for example, cholestanone and methyl ethyl ketone, form colourless dibromides in solution (compare also Linnemann, *Annalen*, 1863, **125**, 307; Lippmann, *Zeitsch. Chem.*, 1869, **5**, 29). The ketone gives negative results with the following reagents for aldehydes: sodium amalgam and diazobenzenesulphonic acid, benzenesulpho-

hydroxamic acid, pyruvic acid, and β-naphthylamine. It yields a peroxide, from which the ketones $C_{13}H_{26}O$ and $C_{11}H_{22}O$ are formed by boiling with water.

The *alcohol*, $C_{15}H_{32}O$, obtained by reducing the ketone with sodium and alcohol, is a colourless, viscid liquid, with b. p. 178—180°/12 mm. or 173—174°/8 mm., D_4^0 0·848, D_4^{20} 0·838, and n_D^{20} 1·44912. The saturated *hydrocarbon*, $C_{15}H_{32}$, occurs in the first fraction obtained by distilling the crude ketone under diminished pressure, and is deprived of the last traces of ketone by repeatedly shaking with three times its volume of glacial acetic acid, in which the ketone is readily soluble. It has b. p. 260·5—263·5°/723 mm. (corr.) or 127—130°/9·5 mm., D_4^0 0·789, D_4^{20} 0·779, and n_D^{20} 1·43322, and is also formed in small quantities when the ketone is reduced with zinc dust and glacial acetic acid. The *olefine*, $CH_2:CH·CHMe·C_{11}H_{23}$, obtained by the action of phosphoric oxide on the alcohol, $C_{15}H_{32}O$, at 60—70°, has b. p. 150—152°/11 mm. or 290°(corr.)/724 mm., D_4^0 0·803 and D_4^{20} 0·790, and combines readily with bromine. Its *ozonide*, $C_{15}H_{30}O_3$, is a viscid oil, with a pale green colour. When the alcohol $C_{15}H_{32}O$ is heated at 150° for an hour with phosphoric oxide, or when the above olefine is heated for several hours at 130° with the anhydride, a product is formed which contains a small amount of a saturated (cyclic) hydrocarbon.

The *ketone*, $C_{13}H_{26}O$, resembles its higher homologue; it has b. p. 168—170°/10 mm. or 288—289°/722 mm., D_4^0 0·865, D_4^{20} 0·848, and is optically inactive. It is not oxidised so readily as its homologue, $C_{15}H_{30}O$. The *oxime*, $C_{13}H_{27}ON$, is a viscid oil, b. p. 196—198°/11 mm. and D_4^0 0·891, and the *semicarbazone*, $C_{14}H_{29}ON_3$, forms slender needles, m. p. 62°. A 94% yield of the ketone is formed by oxidising β-phytol with a glacial acetic acid solution of chromium trioxide in the presence of potassium hydrogen sulphate, and an 82% yield by boiling β-phytol-ozonide with water. It is formed together with the acid $C_{10}H_{20}O_2$ (26—33%) by oxidising the ketone $C_{15}H_{30}O$ with a glacial acetic acid solution of chromium trioxide in the presence of concentrated sulphuric acid. A by-product formed at the same time is the *ether*, $O(C_{10}H_{21})_2$, which has b. p. 228—233°/722 mm. and D_4^0 0·836.

Trihydroxyphytane, $C_{20}H_{39}(OH)_3$, obtained by converting α-phytol dibromide into the acetate and subsequent hydrolysis, is a viscid oil, sparingly soluble in cold methyl alcohol, and when oxidised with chromium trioxide in the presence of glacial acetic and concentrated sulphuric acids yields the *ketone*, $C_{11}H_{22}O$, as a colourless, mobile oil, b. p. 168—170°/8 mm., together with the acid, $C_{14}H_{28}O_2$; its *semicarbazone*, $C_{12}H_{25}ON_3$, crystallises from alcohol in needles, m. p. 68—72°. The same ketone is formed when the product, obtained by the prolonged action of ozone on the ketone $C_{15}H_{30}O$, is boiled with water. The *ketone*, $C_9H_{18}O$, is a limpid oil, with b. p. 168°/10 mm. or 282°/720 mm., and has D_4^0 0·836. Its *semicarbazone* has m. p. 75°.

The olefine *dibromide*, $C_{15}H_{30}Br_2$, is a yellow oil, and, when shaken with silver acetate and glacial acetic acid at the ordinary temperature, yields the *bromoacetyl* derivative, $C_{15}H_{30}BrAc$, as a viscid oil, which reacts with silver acetate at 100°, yielding the *diacetate*, and this on hydrolysis with cold methyl-alcoholic potassium hydroxide yields an

ether of the glycol, $(C_{15}H_{30}\cdot OH)O$, as a brown, viscid oil. The ether, when oxidised with chromium trioxide, glacial acetic and sulphuric acids, yields as intermediate product a carbonyl *compound*, $C_{15}H_{30}O_2$, and ultimately the acid $C_{14}H_{28}O_2$. The same acid is also formed when the olefine ozonide is boiled for five hours with water, but appreciable amounts of the ester, $C_9H_{17}\cdot CO_2\cdot C_{10}H_{21}$, are also formed. The *acid*, $C_{14}H_{28}O_2$, is a colourless, comparatively viscid oil, with b. p. 186—188°/8—9 mm., D_4^0 0·887 and D_4^{20} 0·870. The *silver* salt, $C_{14}H_{27}O_2Ag$, is obtained crystalline by using alcoholic solutions, and has m. p. 186—188°.

The *acid*, $C_{10}H_{20}O_2$, is a colourless, odourless, viscid oil, b. p. 155—158°/11 mm. and 261°/722 mm., D_4^0 0·956, D_4^{20} 0·936, and n_D^{20} 1·45205; it decolorises permanganate in glacial acetic acid solution after a short time. The *silver* salt, $C_{10}H_{19}O_2Ag$, forms a crystalline precipitate, and with benzene forms colloidal solutions. The *ester*, $C_9H_{17}\cdot CO_2\cdot C_{10}H_{21}$, forms a colourless, mobile oil, b. p. 175—176°/11 mm., D_4^0 0·889, and D_4^{20} 0·808. It is hydrolysed by a cold concentrated solution of potassium hydroxide in methyl alcohol. Electrical conductivity measurements of the acid $C_{10}H_{20}O_2$, phytanic acid, and Δ^{β}-phytenic acid were made in aqueous alcoholic solution. The unsaturated acid is a better electrolyte than the saturated acid, and the acid $C_{10}H_{20}O_2$ conducts better than acetic acid.

A distillation flask similar to that described by Michael (Abstr., 1902, i, 70) is recommended for distillations under reduced pressure. Use is made of a column of glass beads, but the capillary tube for introducing bubbles of air is passed through a side-tube fused into the body of the flask. J. J. S.

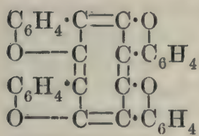
Condensation Products of 2-Coumaranone. KARL FRIES and W. PFAFFENDORF (*Ber.*, 1911, **44**, 114—124. Compare Abstr., 1910, i, 186; also Fries and Fink, Abstr., 1909, i, 42, 44).—By the condensation of 2-coumarone with sodium ethoxide solution in the absence of air, it has been found possible to obtain two isomeric compounds, $C_{16}H_{10}O_3$. The relative amounts of the two vary with the conditions, but so far it has not been found possible to ascertain the conditions which determine the proportions. Neither compound appears to have the hydroxylic structure corresponding with the acetyl derivative already described (Abstr., 1910, i, 186), as they are both very sparingly soluble in alkalis. They are represented as isomeric ketones, and both yield 2 : 1′-diketo-$\Delta^{1,2}$-1 : 2′-dicoumaran ("oxindirubin," "1 : 2-bis-coumaran-indigo"), when mixed with a small amount of bromine in glacial acetic acid solution.

2-*Keto*-1 : 2′-*coumarancoumarone*, $C_6H_4{<}{}^{CO}_{O}{>}CH\cdot C{<}{}^{C_6H_4}_{CH}{>}O$, is the chief product obtained by condensing 2-coumaranone with a hot 3% sodium ethoxide solution, and is also formed by the hydrolysis of the acetate (*loc. cit.*). It crystallises from methyl alcohol in compact, colourless needles, m. p. 116°, and its solution in concentrated sulphuric acid has a yellowish-red colour with a strong yellowish-green fluorescence. Its solutions, especially in the presence of impurities, are

unstable. It yields a somewhat unstable *hydrobromide* in the form of light red needles, and with acetic anhydride and sodium acetate yields the acetate of the tautomeric hydroxy-compound.

The isomeric 2-*keto*-$\Delta^{1:2'}$-*dicoumaran*, $C_6H_4<\begin{matrix}CO\\O\end{matrix}>C:C<\begin{matrix}C_6H_4\\CH_2\end{matrix}>O$, is more readily soluble in acetone, and crystallises from methyl alcohol in brilliant coppery-red plates, m. p. 141°. It is decomposed when boiled for some time with methyl alcohol, yields a yellowish-red *hydrochloride*, and is most readily obtained by condensing 2-coumarone with glacial acetic acid saturated with hydrogen bromide.

When either of the ketones or the acetate, m. p. 106°, is heated for eight hours at 100° with a saturated solution of hydrogen chloride in glacial acetic acid, a *product*, $C_{32}H_{16}O_4$, is obtained, which crystallises from xylene in flesh-coloured needles. These are not molten at 340°, but sublime in reddish plates with a metallic lustre. The annexed formula is suggested. Nitric acid converts it into a deep black-coloured substance, the acetic acid solution of which has a reddish-violet colour.



By the condensation of 5-methylcoumaranone with sodium ethoxide, only one product is obtained, namely, 2-*keto*-5 : 5'-*dimethyl*-$\Delta^{1:2'}$-*dicoumaran*, $C_{18}H_{14}O_3$. This crystallises from alcohol in yellow prisms, m.p. 156° (when quickly heated), and is readily oxidised to 5:5'-dimethyl-leuco-oxindirubin. It undergoes decomposition when heated alone or with glacial acetic acid. The *product*, $C_{36}H_{24}O_4$, obtained by heating the acetate, m. p. 133° (*loc. cit.*), with a saturated solution of hydrogen chloride in glacial acetic acid, crystallises from xylene in pale red needles, which melt above 340°. When rubbed with a little nitric acid it yields a blue-black compound, which dissolves in glacial acetic acid to brilliant violet-blue coloured solutions.

2 : 1'-Dihydroxy-1 : 2'-dicoumarone ("leuco-oxindirubin") yields a *phenylhydrazone*, $C_{22}H_{16}O_3N_2$, which crystallises from glacial acetic acid in pale red needles, m. p. 179°, and when hydrolysed with hydrochloric acid yields oxindirubin.

The *acetyl* derivative of 2 : 1'-dihydroxy-1 : 2'-dicoumarone, $C_{18}H_{12}O_5$, crystallises in glistening plates, m. p. 198°; when hydrolysed with alkalis it yields the *leuco*-compound, but with hydrochloric acid yields oxindirubin.

The *phenylhydrazone* of 2 : 1'-dihydroxy-5 : 5'-dimethyl-1 : 2'-dicoumarone, $C_{21}H_{20}O_3N_2$, forms red needles, m. p. 163°. The *oxime*, $C_{18}H_{15}O_4N$, crystallises from methyl alcohol in yellow needles, m. p. 194°, and the *acetyl* derivative, $C_{20}H_{16}O_5$, in yellow prisms, m. p. 200°.

J. J. S.

Oxindigo [2 : 2-Diketo-$\Delta^{1:1'}$-dicoumaran]. KARL FRIES and A. HASSELBACH (*Ber.*, 1911, 44, 124—128).—So far it has not been found possible to obtain "oxindigo" by the alkaline oxidation of 2-coumaranone, or from halogen derivatives of coumaranone (compare Abstr., 1897, i, 424; 1901, i, 94; 1909, i, 44, 174).

Attempts to prepare the oxygen compound of the action of

ammonium sulphide on *p*-dimethylaminoanildiketocoumaran were also unsuccessful.

By the condensation of the anil derivative with 2-coumaranone in boiling xylene, a product, $C_{24}H_{20}O_4N_2$, is formed, and this, when hydrolysed by means of a mixture of glacial acetic and concentrated sulphuric acid at the ordinary temperature, yields amino-dimethylaniline and "oxindigo."

3-*Keto*-2-p-*dimethylaminoanilcoumaran*,

$$C_6H_4<^{CO}_{-O-}>C:N\cdot C_6H_4\cdot NMe_2,$$

prepared by the action of an alcoholic solution of 2-coumaranone on an alcoholic solution of *p*-nitrosodimethylaniline in the presence of 2*N*-sodium hydroxide solution at 3°, crystallises from benzene in large prisms with a blue-black lustre, or from alcohol in dark brown, glistening needles, m. p. 185°. It is hydrolysed by strong acids to *p*-aminodimethylaniline and *o*-hydroxyphenylglyoxylic acid.

The condensation *product*, $C_{24}H_{20}O_4N_2$, probably

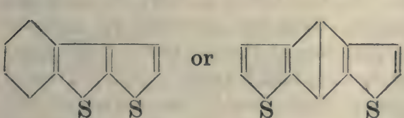
$$C_6H_4<^{CO}_{-O-}>C(NH\cdot C_6H_4\cdot NMe_2)\cdot CH<^{CO}_{-O-}>C_6H_4,$$

crystallises from a mixture of benzene and light petroleum in flat prisms with a bronzy lustre, m. p. 203° (decomp.), after sintering at 190°. The yield is 30% of the theoretical, and the product dissolves in alkali hydroxides, yielding reddish-brown solutions.

2 : 2-*Diketo*-$\Delta^{1:1'}$-*dicoumaran* ("*oxindigo*," "1 : 1-*dicoumarone-indigo*"), $C_6H_4<^{CO}_{-O-}>C:C<^{CO}_{-O-}>C_6H_4$, crystallises from glacial acetic acid or from xylene in long prisms, with an intense lemon-yellow colour. It has m. p. 272° after sintering at 250°, and its solution in concentrated sulphuric acid has a yellowish-red colour.

It is decomposed by alcoholic sodium hydroxide solution, and even by sodium carbonate in the presence of alcohol. J. J. S.

A New Thiophen Compound, $C_{10}H_6S_2$, and Some of its Derivatives. M. LANFRY (*Compt. rend.*, 1911, **152**, 92—94).—The tarry product obtained when a mixture of sulphur and naphthalene vapour is passed through a red-hot iron tube contains 0·2—0·4% of a compound crystallising in ruby-red leaflets or clinorhombic prisms.



The substance has m. p. 118·5° (corr.), b. p. 345°, and in composition approximates to the formula $C_{10}H_6S_2$; it is supposed to be *benzdithiophen* (annexed formulæ). It gives the thiophen reaction with sulphuric acid and isatin. The *bromo*-derivative, $C_{10}S_2H_2Br_4$, crystallises in silky, orange needles, m. p. 247—248°. The *tetranitro*-derivative, $C_{10}S_2H_2(NO_2)_4$, was obtained as an orange powder, decomposing at 300°; it has well-marked acid characters, and forms highly-coloured compounds with cyclic hydrocarbons.

On treating benzdithiophen with hydrogen peroxide in acetic acid solution, it yields in the first place a *compound*, $C_{10}H_6O_2S_2$, slender

rose-yellow needles, m. p. 130°, having the properties of a *p*-diphenol. On further oxidation, a second *compound*, $C_{10}H_6O_4S$, is formed; this crystallises in radiating, red needles, m. p. about 125°; it is insoluble in aqueous alkalis, and develops no coloration with sulphuric acid and isatin. W. O. W.

Silicotungstates of Coniceine, Sparteine, and Atropine. MAURICE JAVILLIER (*Bull. Sci. Pharm.*, 1910, 315—320. Compare Abstr., 1899, ii, 456; 1909, ii, 450).—*Coniceine silicotungstate*,

$$12WO_3,SiO_2,2H_2O,4C_8H_{17}N + 3H_2O,$$

prepared by adding potassium silicotungstate to an aqueous solution of coniceine tartrate, is an amorphous substance which becomes anhydrous at 120°. It is soluble in boiling water; 100 c.c. of water at 15° dissolve about 0·02 gram of the salt.

Sparteine silicotungstate, $12WO_3,SiO_2,2H_2O,2C_{15}H_{26}N_2 + 7H_2O$, is amorphous, and loses $6H_2O$ at 120°. The precipitation of this salt is visible in aqueous solutions containing 0·0002% of sparteine, and, consequently, may be employed in estimating the alkaloid.

Atropine silicotungstate, $12WO_3,SiO_2,2H_2O,4C_{17}H_{23}O_3N + 4H_2O$, becomes anhydrous at 120°. It is less easy to obtain pure than the foregoing, owing to a tendency to undergo hydrolysis. Advantage has been taken of its sparing solubility (less than 1 in 40,000) to estimate atropine in pharmaceutical preparations. W. O. W.

Preparation of Alkyl Halides and Alkyl Nitrates of Tropeine and Scopoleine Alkaloids. A. GERBER (D.R.-P. 228204).—*Methyl-atropinium methosulphite*, $C_{17}H_{23}O_3NMe{\cdot}SO_3Me$, is prepared by heating atropine with methyl sulphite and methyl alcohol in a sealed tube at 100°; the *platinichloride*, $(C_{17}H_{23}O_3NMeCl)_2PtCl_4$, forms orange-coloured leaflets. *Atropine methobromide*, m. p. 220°, and *atropine methonitrate* are formed respectively by evaporating the foregoing compound with aqueous potassium bromide, or with potassium nitrate; these compounds are soluble in water or alcohol, sparingly so in ether or acetone. F. M. G. M.

Dihydroberberine. JOHANNES GADAMER (*Arch. Pharm.*, 1910, **248**, 670—681).—Faltis' evidence for the view that the action of potassium hydroxide on berberine results in the formation of oxyberberine and tetrahydroberberine (Abstr., 1910, i, 698) is reviewed and criticised, and further facts are brought forward in support of the author's opinion that in this reaction oxyberberine and dihydroberberine are formed (Abstr., 1902, i, 173, 555; 1905, i, 369; Freund and Beck, 1905, i, 151). Faltis' observation that by the action of zinc and acetic acid on oxyberberine, the latter is rendered colourless, could not be confirmed.

Dihydroberberine hydrochloride, prepared as already described (*loc. cit.*), crystallises with $4H_2O$, but readily loses $1H_2O$ on drying in a desiccator. Dihydroberberine is less basic than tetrahydroberberine, and is less easily removed than the latter from solution in ether by agitation with dilute hydrochloric acid. Tetrahydroberberine is resolved by crystallisation of the *d*-bromocamphorsulphonate into *d*- and *l*-canadines, but repetition of a similar fractional crystallisation

of dihydroberberine *d*-bromocamphorsulphonate (Abstr., 1902, i, 173) showed that no resolution of this base took place, although tetrahydroberberine was again easily resolved, either alone or in admixture with dihydroberberine.

Dihydroberberine furnishes a *methiodide*, m. p. 205°, which dissolves in water, forming a yellow solution giving no precipitate with ammonia, but forming a white precipitate with much sodium hydroxide, the liquid at the same time developing a violet fluorescence; the precipitate is not dissolved by ether. *Tetrahydroberberine methiodide*, m. p. 245—250°, is colourless and soluble with difficulty. Oxyberberine forms an additive product with methyl sulphate.

Dihydroberberine is more poisonous to rabbits than tetrahydroberberine. T. A. H.

Corydalis Alkaloids. V. *R*-Corydaline and Phenylberberine. JOHANNES GADAMER (*Arch. Pharm*, 1910, **248**, 681—695).—A description of direct and indirect attempts made to resolve optically inactive corydaline, m. p. 135°, into optically active forms (Abstr., 1902, i, 306; 1905, i, 463).

[With ERNST STEINBRECHER.]—Attempts to effect resolution by fractionation of the tartrate, quinate, and *d*-bromocamphorsulphonate were unsuccessful. Natural *d*-corydaline does not give a crystalline salt with the last-mentioned acid.

Attempts were then made to effect the resolution of α-methyldihydroberberine (Freund and Beck, Abstr., 1905, i, 151), and to reduce the *d*- and *l*-isomerides thus obtained, so producing active forms, which should differ from corydaline only in containing a dioxymethylene group in place of two methoxyls, and should therefore correspond with the *d*- and *l*-corydalines and to *d*- and *l*-*meso*corydaline (compare Freund and Mayer, Abstr., 1907, i, 633). The resolution of *r*-α-methyldihydroberberine could not, however, be effected, and this was also the case for phenylberberine.

Oxyberberine treated with magnesium ethyl iodide in benzene solution, with dimethylaniline as a catalyst, was recovered for the most part unchanged, but small quantities of methylnoroxyberberine (Faltis, Abstr., 1910, i, 698) and of a non-basic *substance*, m. p. 165—166°, separating from alcohol in bright yellow crystals, were obtained.

Oxyberberine reacts with magnesium phenyl bromide in ether to form (1) a tertiary *base*, which may be either a phenyltetrahydroberberine or diphenyldihydroberberine, and (2) *phenylberberine*. The latter furnishes a *hydrochloride*, m. p. 255—257° (decomp.), which separates from alcohol or water in brownish-yellow crystals. The *aurichloride*, m. p. 215—216° (decomp.), forms long, brown needles from alcohol containing hydrochloric acid. The *acid sulphate* softens at 270°, but does not melt even at 278°, and separates from dilute sulphuric acid in compact, yellow crystals. The *nitrate*, m. p. 268—270° (decomp.), is deposited from alcohol in compact, brown crystals.

On reduction with zinc and dilute sulphuric acid, phenylberberine hydrochloride yields *phenyltetrahydroberberine*, m. p. 222°, which

separates from a mixture of chloroform and alcohol in compact, almost colourless crystals, and may also be obtained by reduction of phenyldihydroberberine. The latter, prepared by Freund and Beck's method (Abstr., 1905, i, 151), on oxidation with iodine in alcohol furnished iso*phenylberberine*, which gives a *hydrochloride*, m. p. 275—278° (decomp.), separating from water in silky, bright yellow crystals. The *aurichloride* forms reddish-brown, short needles, sinters at 250°, but does not melt at 280°; along with it was produced a second gold salt, m. p. 223—225°, which may be impure phenylberberine aurichloride (see above), since on decomposition with hydrogen sulphide it yielded some phenylberberine hydrochloride. This phenylberberine is probably produced in the initial oxidation along with *iso*phenylberberine. The latter, on reduction, yielded a varnish from which no crystalline derivative could be obtained. The relationship between phenylberberine and *iso*phenylberberine is uncertain, and it is regarded as improbable that the difference is due to hydrogenation of a different pyridine nucleus in each case. T. A. H.

Preparation of Curarine. RUDOLF BOEHM (*Pflüger's Archiv*, 1910, **136**, 203—207).—The action of curare is so uncertain, because commercial specimens contain other substances, in addition to its most active constituent curarine. The best kinds of curare contain only 3 to 9% of this alkaloid. Very small doses of curarine produce marked results. The methods of separating it from curare have been dealt with *in extenso* in the author's previous writings (Abstr., 1887, 1125; 1898, i, 283), and are briefly given in the present paper. W. D. H.

Preparation of Alkylhalogen Derivatives of Morphine Alkaloids. A. GERBER (D.R.-P. 228247).—The halogen double salts of the alkaloids and their quaternary compounds obtained by the action of alkyl halides and methyl sulphate have been previously described (Abstr., 1905, i, 542, 658; 1906, i, 530, 877; 1908, i, 452), and the work has now been extended to the products obtained with methyl sulphite.

Methylmorphinium methosulphite, $C_{17}H_{19}O_3NMe\cdot SO_3Me$, is prepared by heating morphine with methyl sulphite and methyl alcohol in a sealed tube at 100°, and subsequently evaporating in a vacuum; the amorphous, faintly coloured, hygroscopic product is rendered crystalline by dissolving in absolute alcohol and precipitating with ether; when evaporated with a saturated solution of potassium bromide, it is converted into morphine methobromide (m. p. 260°).

Methylnarcotinium methosulphite has similar properties, and is analogously prepared from narcotine; its *platinichloride*,

$$(C_{22}H_{23}O_7NMeCl)_2PtCl_4,$$

forms small, orange crystals.

*Methylcodeinium methosulphite, methyl*apo*morphinium methosulphite, methylthebanium methosulphite*, with their respective *methobromides*, were also prepared; thebaine methobromide has m. p. 185°.

F. M. G. M.

Strychnine and Brucine. II. Roberto Ciusa and G. Scagliarini (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 501—505. Compare Abstr., 1910, i, 583).—When cacothelin is suspended in water acidified with hydrobromic acid and treated with bromine water until it has all dissolved, it is converted into the *hydrobromide* of an acid, $C_{19}H_{22}O_6N_2,HBr,2H_2O$, which is obtained in yellow crystals by the evaporation of the solution. The free acid, $C_{19}H_{22}O_6N_2,2H_2O$ (compare Hanssen, Abstr., 1887, 505), forms scales having a nacreous lustre. It is not toxic. The *platinichloride*, $(C_{19}H_{22}O_6N_2),H_2PtCl_6$, obtained in presence of hydrochloric acid, crystallises in small, yellow prisms. R. V. S.

Identity of Vernine and Guanosine and Notes on Vicine and Convicine. Ernst Schulze and G. Trier (*Zeitsch. physiol. Chem.*, 1910, **70**, 143—151. Compare Abstr., 1910, ii, 645).—The pentose (compare Schulze and Castoro, Abstr., 1904, ii, 506) obtained by the hydrolysis of vernine yields *l*-arabinose-*p*-bromophenylosazone (Levene and Jacobs, Abstr., 1909, i, 858), and is presumably *d*-ribose. A detailed comparison of vernine with Levene and Jacobs' guanosine (Abstr., 1910, i, 620) has proved that the two are identical.

The following formulæ are suggested for vicine and convicine, namely, $C_{20}H_{36}O_{15}N_8$ and $C_{20}H_{28}O_{16}N_6,2H_2O$.

The hydrolysis of vicine is represented by the equations:

$$(1)\ C_{20}H_{36}O_{15}N_8 + H_2O = \underset{\text{Divicin.}}{C_8H_{14}O_4N_8} + \underset{\text{Hexoses.}}{2C_6H_{12}O_6}$$

$$(2)\ C_8H_{14}O_4N_8 + 4H_2O = C_8H_{10}O_8N_4 + 4NH_3,$$

and that of convicine by the equation:

$$C_{20}H_{28}O_{16}N_6,2H_2O + 4H_2O = \underset{\text{Alloxanthin.}}{C_8H_6O_8N_4,2H_2O} + 2C_6H_{12}O_6 + 2NH_3$$

(compare Ritthausen, Abstr., 1881, 1158; 1899, i, 715).

The two compounds are thus glucosides formed by the condensation of hexoses with pyrimidine derivatives. J. J. S.

Indole in Coal Tar. Rudolf Weissgerber (*Ber.*, 1910, **43**, 3520—3528).—The *sodium* derivative of indole, $C_6H_4<\genfrac{}{}{0pt}{}{-CH}{NNa}>CH$, is obtained in the form of a brown, amorphous mass, m. p. 140°, by heating indole with sodamide at 150—160°, or with sodium at 170—180°; it reacts with methyl iodide, yielding 1-methylindole, together with small quantities of 2-methylindole and 3-methylindole.

On warming with benzoyl chloride in benzene solution, it yields *benzoylindole*, $C_6H_4<\genfrac{}{}{0pt}{}{-CH}{NBz}>CH$; the latter crystallises from alcohol in compact, rhombic plates, m. p. 67—68°, b. p. 213°/16 mm., and is readily hydrolysed by aqueous sodium hydroxide.

The *potassium* derivative of indole is obtained as a light-coloured mass by heating indole with potassium hydroxide.

The formation of the potassium compound furnishes a ready means of separating indole from coal tar. The fraction, b. p. 240—260°, freed from phenols and bases by shaking with alkali hydroxide and dilute sulphuric acid is heated with potassium hydroxide at 190—200°,

the unattacked oil removed by washing with benzene, and the potassium indole decomposed by water; the separation may also be effected by means of sodium or sodamide.

The crude indole may be purified by converting it into the bisulphite compound (Hesse, Abstr., 1900, i, 48), or into the sodium salt of indolecarboxylic acid (compare Zatti and Ferratini, Abstr., 1890, i, 292), by heating with sodium at 190—200° in a stream of carbon dioxide. The free acid obtained from the sodium salt by acidification loses carbon dioxide when heated in a vacuum at 230—250° and yields indole. F. B.

Preparation of Halogenindoxylic Acids and their Esters. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 226689).—The conversion by alkalis of phenylglycine-*o*-carboxylic acids into derivatives of indoxyl has been described (compare Abstr., 1908, i, 974, 1019), and it is now found that the reaction can be applied successfully to halogenated derivatives of the acid.

Methyl 5 : 7-*dichloroindoxylcarboxylate*, $C_6H_2Cl<\substack{-NH-\\C(OH)}>C\cdot CO_2Me$, colourless needles, m. p. 195°, is prepared by boiling *dimethyl* 4 : 6-*dichlorophenylglycine*-2-*carboxylate*, m. p. 77—78°, in toluene solution with sodium or sodium methoxide; the toluene can be replaced by other indifferent solvents.

Dimethyl 6-*chloro*-4-*bromophenylglycine*-2-*carboxylate*, m. p. 81—83° (obtained from 6-chloro-4-bromophenylglycine-2-carboxylic acid, m. p. 238°, in the usual manner), yielded on similar treatment *methyl* 7-*chloro*-5-*bromoindoxylcarboxylate*, $C_6H_2ClBr<\substack{-NH-\\C(OH)}>C\cdot CO_2Me$, long needles, m. p. 203—205°.

Methyl 4 : 6-*dichlorophenylglycine*-2-*carboxylate*, colourless needles, m. p. 133—134°, on treatment with sodium ethoxide yielded *sodium* 5 : 7-*dichloroindoxylcarboxylate*, a yellow powder which is readily converted into 5 : 7 : 5′ : 7′-tetrachloroindigotin by the action of air and water. F. M. G. M.

Betaine Formation and Steric Hindrance. ALFRED KIRPAL (*Monatsh.*, 1910, 31, 969—979. Compare Abstr., 1908, i, 679).—Nicotinic, *iso*nicotinic, and cinchomeronic acids interact with chloroacetic acid in neutral solution, giving almost theoretical yields of the corresponding betaines; picolinic and quinolinic acids, under the same conditions, react incompletely, whilst dipicolinic acid remains unchanged. The author suggests that these results may be explained on the assumption that the carboxyl group in the α-position exerts a negative influence on the nitrogen atom, which therefore shows less tendency to assume the quinquevalent condition. This explanation is, however, not applicable to quinaldine and 2 : 6-dimethylpyridine, both of which, on treatment with chloroacetic acid, do not yield betaine, but are converted into their hydrochlorides; the non-formation of betaines in these cases is referred to steric influences.

iso*Nicotinic acid betaine*, $C_8H_7O_4N$, prepared by heating *iso*nicotinic

acid and chloroacetic acid in faintly alkaline, aqueous solution, crystallises in needles, m. p. 262° (decomp.).

Nicotinic acid betaine forms monoclinic prisms or octahedral crystals, and has m. p. 190° (decomp.).

Picolinic acid betaine crystallises in short, pointed prisms, m. p. 165° (decomp.); the *hydrochloride* has m. p. 181°.

Cinchomeronic acid betaine, $C_9H_7O_6N$, forms rhombic plates, m. p. 180° (decomp.).

Quinolinic acid betaine, $C_9H_7O_6N,H_2O$, crystallises in colourless prisms, which, when heated at 100°, lose their water of crystallisation and carbon dioxide, yielding nicotinic acid betaine; the same decomposition also takes place on boiling its aqueous solution; the *hydrochloride* is readily hydrolysed, aqueous solutions rapidly depositing the free betaine.

α-Picolinebetaine, $C_8H_9O_2N$, prepared by heating α-picoline with chloroacetic acid on the water-bath and isolated by means of its platinichloride, crystallises in colourless, hygroscopic needles, which turn brown at 100° and decompose at 162°; the *platinichloride* forms yellow prisms, m. p. 212° (decomp.); the *hydrochloride* has m. p. 188° (decomp.). F. B.

Derivatives of 2-Phenylquinoline. II. ERNST MURMANN (*Monatsh.*, 1910, **31**, 1303—1306. Compare Abstr., 1892, 1003).—Disulphonic acids can be obtained by heating 1-phenylquinoline with four times its weight of commercial fuming sulphuric acid on the water-bath until a test drop gives no crystals (monosulphonic acid) when heated with five drops of water and no turbidity on addition of aqueous ammonia.

The mass is diluted with five times its weight of water, and a small amount of monosulphonic acid separates during the course of a day. After further dilution, boiling with animal charcoal, and neutralising with barium carbonate, crystals of a *barium* salt,

$$C_{15}H_9O_6NS_2Ba,6H_2O,$$

in the form of long, colourless needles, are obtained. The *calcium* salt, $C_{15}H_9O_6NS_2Ca,6H_2O$, forms slender, yellow needles, sparingly soluble in water, and the *zinc* salt crystallises with $5H_2O$ in large, felted needles.

The filtrate from the barium salt contains an isomeric salt, which is sparingly soluble in alcohol, and crystallises with $12H_2O$. The first barium salt, when fused with potassium hydroxide, yields a red *phenol*, m. p. 140—141°. J. J. S.

Formation of Acyl Derivatives of Phenylhydrazine in Aqueous Solution. STEPHAN JAROSCHY (*Monatsh.*, 1910, **31**, 951—967).—The phenylhydrazides of formic, acetic, propionic, butyric, and *iso*butyric acids are readily formed by heating the acids with phenylhydrazine in aqueous solution. The relative velocities of formation of these hydrazides under various conditions at 100° have been investigated by estimating the amount of unchanged acid by titration with barium hydroxide. With the same concentration of acid

and of base, it is found that the rates of formation stand in the same order as the magnitude of the dissociation constants of the acids.

The effect of temperature was studied in the case of the formyl derivative. Increase of temperature is accompanied by an increase in the relative velocity, and the same effect is produced by increasing the concentration of the acid.

The addition of a small quantity of hydrochloric acid was found to diminish the rate of formation of the acetyl derivative. The author suggests that this is to be referred to the diminution in the ionisation of the acetic acid; on this assumption, the acylation is due to the anions.

F. B.

Oxidation of Methyluracil. ROBERT BEHREND and KARL STRUVE (*Annalen*, 1910, **378**, 153—169. Compare Behrend and Dietrich, Abstr., 1900, i, 120; Behrend and Grünewald, Abstr., 1902, i, 834; Behrend and Fricke, Abstr., 1903, i, 739; Behrend and Osten, Abstr., 1906, i, 309; Behrend and Hufschmidt, Abstr., 1906, i, 310; Hobel, Abstr., 1907, i, 557; Offe, *ibid.*, 645).—When oxidised with potassium ferricyanide in ammoniacal solution, methyluracil yields the amide of uracilcarboxylic acid: $CO<\begin{matrix}NH—CO\\NH\cdot CMe\end{matrix}>CH + NH_3 + 3O = CO<\begin{matrix}NH——CO\\NH\cdot C(CO\cdot NH_2)\end{matrix}>CH + 2H_2O$. This appears to be the first instance recorded of the oxidation of a $-CH_3$ to a $-CO\cdot NH_2$ group. The reaction does not consist in the oxidation of the methyl to a carboxylic group and the conversion of the latter into the $-CO\cdot NH_2$ group by means of ammonia, as it is shown that a temperature of 240° is required for the latter reaction. It is possible that an aldehyde group is first formed, and that this yields an aldehyde-ammonia, $-CH<\begin{matrix}OH\\NH_2\end{matrix}$, which is then oxidised to the $-CH<\begin{matrix}O\\NH_2\end{matrix}$ group. When the oxidation takes place in the presence of potassium hydroxide the product is uracilcarboxylic acid.

In the preparation of the amide, the mixture is heated at 50—60° for five to six hours and allowed to cool, when potassium ferrocyanide separates; this is removed, and the filtrate heated until all the ammonia is driven off and an odour of hydrogen cyanide is noticed. The solution is filtered hot and kept for one to two days at the ordinary temperature, when methyluracil separates as octahedra or needles, and in the course of a week or so the amide separates in a crystalline form. It is most readily freed from uracil by conversion into its sparingly soluble *potassium* derivative, $C_5H_4O_3N_3K,2H_2O$, which crystallises from hot water in well-developed prisms. Its solution has an alkaline reaction. The *amide*, $C_5H_5O_3N_3,H_2O$, crystallises in small, lancet-shaped plates, dissolves in 110 parts of boiling water, and in 2000 parts of water at 20°. When boiled with alkalis, it yields *uracil-carboxylic acid*, $CO<\begin{matrix}NH——CO\\NH\cdot C(CO_2H)\end{matrix}>CH,H_2O$, in the form of rhombic plates, which lose their water of hydration at 120°. The anhydrous compound decomposes above 300° without melting. The hydrated compound dissolves in 70 parts of water at 100° and in 500 parts at 18°.

The addition of acetic acid to a solution of the carboxylic acid in potassium hydroxide solution precipitates *potassium uracilcarboxylate*, $C_5H_3O_4N_2K$. The *ammonium* salt, $C_5H_7O_4N_3,H_2O$, crystallises in small, six-sided plates. The acid is identical with the product obtained by hydrolysing the ester described by Müller (Abstr., 1897, i, 549).

When methyluracil is oxidised with potassium ferricyanide in the presence of potassium hydroxide solution, it is best to leave the mixture for twenty days at the ordinary temperature and then to acidify with acetic acid, when potassium uracilcarboxylate is precipitated.

It has not been found possible to oxidise the carboxylic acid with potassium ferricyanide, but with permanganate (3O) at 15° the acid yields oxaluric and oxalic acids. J. J. S.

Oxidation of α- and β-Dimethyluracils. PAUL HENKEL (*Annalen*, 1910, **378**, 170—187. Compare Behrend and Grünewald, Abstr., 1902, i, 834).—The oxidation of α- and β-dimethyluracils is analogous to that of methyluracil (compare table given by Osten, *Annalen*, 1905, **343**, 151). Methylparabanic acid can be isolated from the oxidation products of both compounds, under conditions such that its formation from methyloxaluric acid is excluded. The two dimethyluracils have been transformed into corresponding α- and β-trihydroxydimethyldihydrouracils by Osten's method (Abstr., 1906, i, 309). These hydroxy-derivatives exist in only one form, whereas the corresponding trihydroxymethyldihydrouracil exists in two forms (Abstr., 1908, i, 840). Although it has not been found possible to isolate an acetylmethylallanturic acid by the action of alkali on the trihydroxy-derivatives, it is shown that a conversion of the six-membered ring into a five-membered ring must take place under the influence of alkalis, since, when oxidised with permanganate in the presence of excess of potassium hydrogen carbonate, the α-trihydroxy-derivative yields methylparabanic acid together with methyloxaluric acid, but no trace of acetylmethylcarbamide. Trihydroxy-β-dimethyldihydrouracil is oxidised much less readily, and under similar conditions yields *s*-acetylmethylcarbamide together with methyloxaluric acid and methylparabanic acid; but when the solution of the hydroxy-compound is left in contact with the potassium hydrogen carbonate for twenty-four hours before the addition of the permanganate, the products obtained are methylparabanic acid and methyloxaluric acid. Acetylmethyloxaluric acid is not formed during the oxidation in the presence of the carbonate.

Nitro-α-dimethyluracil (5-*nitro*-2:6-*dioxy*-3:4-*dimethyldihydropyrimidine*), $CO<\begin{matrix}NH\text{—}CO\\NMe\cdot CMe\end{matrix}>C\cdot NO_2$, prepared by Osten's method (*loc. cit.*), crystallises from water in yellow plates, m. p. 249—250°, and when reduced by Behrend and Grünewald's method (*loc. cit.*) yields the corresponding *amino*-derivative, $C_6H_9O_2N_3$, in the form of yellow crystals, m. p. 281—282°.

Trihydroxy-α-dimethyldihydrouracil (4:5:5-*trihydroxy*-2:6-*dioxy*-3:4-*dimethyldihydropyrimidine*), $CO<\begin{matrix}NH\text{————}CO\\NMe\cdot CMe(OH)\end{matrix}>C(OH)_2$, obtained by oxidising the amino-α-dimethyluracil with bromine water at low temperatures, crystallises when its aqueous solution is concentrated

at the ordinary temperature under 4 mm. pressure, and decomposes at 120°. When heated at 70—80° for fifteen minutes with ethyl alcohol, it yields the 5 : 5-*diethoxy*-derivative, $CO<\begin{matrix}NH\text{———}CO\\NMe\cdot CMe(OH)\end{matrix}>C(OEt)_2$, which crystallises from alcohol, and has m. p. 114—116°.

Nitro-β-dimethyluracil (*5-nitro-2 : 6-dioxy-1 : 4-dimethyldihydropyrimidine*), $CO<\begin{matrix}NMe-CO\\NH\cdot CMe\end{matrix}\geqslant C\cdot NO_2$, crystallises from water in pale yellow prisms, m. p. 229—230° (decomp.); the corresponding *amino*-derivative has m. p. 256—257° (decomp.), and *trihydroxy-β-dimethyldihydrouracil* (*4 : 5 : 5-trihydroxy-2 : 6-dioxy-1 : 4-dimethyldihydropyrimidine*), $CO<\begin{matrix}NMe\text{———}CO\\NH\cdot CMe(OH)\end{matrix}>C(OH)_2$, crystallises from dilute acetic acid, and decomposes at 133°.

Bromo-β-dimethyluracil, $CO<\begin{matrix}NMe\cdot CO\\NH\cdot CMe\end{matrix}\geqslant CBr$, is sometimes formed as a by-product; it has m. p. 243°. 4-*Hydroxy*-5 : 5-*diethoxy*-2 : 6-*dioxy*-1 : 4-*dimethyldihydropyrimidine*, $C_{10}H_{18}O_5N_2$, crystallises from alcohol, has m. p. 124—126° (decomp.), and dissolves in 20 parts of cold absolute alcohol.

Methylparabanic acid is readily transformed into methyloxaluric acid when its alcoholic solution is made alkaline with *N*/5-alcoholic potash and kept for an hour.

It has not been found possible to obtain either of the above-mentioned nitro-derivatives by the action of methyl iodide and alkali on nitromethyluracil. J. J. S.

Action of Potassium Permanganate and of Bromine on 1 : 4 : 5-Trimethyluracil. KARL BREMER (*Annalen*, 1910, **378**, 188—209).—By analogy with methyluracil (Abstr., 1906, i, 310) it was thought probable that by the oxidation of 1 : 4 : 5-trimethyluracil with cold permanganate, methylacetylcarbamide and pyruvic acid would be formed, and that with warm permanganate, acetyldimethylhydantoin or its oxidation products would be obtained. Actual experiment has shown that the products are the same at both temperatures, using 2 atoms of oxygen; in both cases only acetylmethylcarbamide and a syrup are formed. No trace of pyruvic acid can be detected in the syrup, and the only product so far isolated from the syrup is oxalic acid. Dihydroxytrimethyldihydrouracil has been prepared by Behrend, Osten, and Beer's method (Abstr., 1906, i, 309), but it has not been settled definitely whether the compound has the constitution of the uracil (1) or whether it is the isomeric acetyldimethyl hydantoin (2).

(1) $CO<\begin{matrix}NMe\text{———}CO\\NH\cdot CMe(OH)\end{matrix}>CMe\cdot OH$. (2) $CO<\begin{matrix}NMe\cdot CO\\NH-CMe\cdot CMe(OH)_2\end{matrix}$.

In favour of the latter formula are the facts that it is not readily oxidised, and does not appear to be affected by alkalis.

Attempts to oxidise 1-phenyl-4 : 5-dimethyluracil were unsuccessful, owing to the slight solubility of the compound in water.

Behrend and Hennicke's method (Abstr., 1906, i, 314) for the preparation of thiontrimethyluracil gives a 25% and not an 80% yield. A 45—50% yield is obtained when a mixture of equivalent

quantities of methyl thiocarbimide and ethyl β-amino-α-methyl crotonate is heated to 55—60° and then kept for twenty-four hours in an ice chest; after removing the crystals, the filtrate is heated to 70°, and on cooling gives a further crop of crystals. The desulphurisation is accomplished most readily by heating the compound in a reflux apparatus with 65% sulphuric acid for about forty-five minutes at 150—160° and subsequent dilution with three times the volume of water. The yield of trimethyluracil is 80%; it crystallises from hot water, and has m. p. 222—223°.

1-Phenyl-4 : 5-dimethyluracil, $C_{12}H_{12}O_2N_2$, is formed when ethyl phenylcarbamidomethylcrotonate (Abstr., 1901, i, 136), prepared from ethyl β-amino-α-methylcrotonate and phenylcarbimide, is hydrolysed with 5% potassium hydroxide solution and the solution acidified with hydrochloric acid; it has m. p. 235°.

4-*Bromo*-5-*hydroxy*-1 : 4 : 5-*trimethyldihydrouracil*,

$$\mathrm{CO}<\begin{matrix}\mathrm{NMe}\text{——}\mathrm{CO}\\ \mathrm{NH\cdot CMeBr}\end{matrix}>\mathrm{CMe\cdot OH},$$

obtained by the action of water and an excess of bromine on trimethyluracil at the temperature of the water-bath, crystallises from hot water in needles, m. p. 127° after sintering at 120°. When heated with alcohol, or by itself at 95°, and then at 115°, it loses water and yields 4-*bromo*-1 : 4-*dimethyl*-5-*methylenedihydrouracil*,

$$\mathrm{CO}<\begin{matrix}\mathrm{NMe}\text{——}\mathrm{CO}\\ \mathrm{NH\cdot CMeBr}\end{matrix}>\mathrm{C{:}CH_2},$$

which crystallises from benzene or dilute alcohol, and has m. p. 195° after sintering at 170°. This unsaturated compound reacts with bromine water, yielding 4-*bromo*-5-*hydroxy*-1 : 4-*dimethyl*-5-*bromomethyldihydrouracil*, $\mathrm{CO}<\begin{matrix}\mathrm{NMe}\text{——}\mathrm{CO}\\ \mathrm{NH\cdot CMeBr}\end{matrix}>\mathrm{C(CH_2Br)\cdot OH}$, m. p. 150—151° after sintering at 145°, and this, when heated at 90—100° for three hours, yields 4-*bromo*-1 : 4-*dimethyl*-5-*bromomethylenedihydrouracil*, $\mathrm{CO}<\begin{matrix}\mathrm{NMe}\text{——}\mathrm{CO}\\ \mathrm{NH\cdot CMeBr}\end{matrix}>\mathrm{C{:}CHBr}$, in the form of well-developed needles, m. p. 175—178°, which again react with bromine water, yielding 4-*bromo*-5-*hydroxy*-1 : 4-*dimethyl*-5-*dibromomethyldihydrouracil*, $\mathrm{CO}<\begin{matrix}\mathrm{NMe}\text{——}\mathrm{CO}\\ \mathrm{NH\cdot CMeBr}\end{matrix}>\mathrm{C(CHBr_2)\cdot OH}$, as colourless crystals.

Dibromohydroxymethyldihydrouracil does not yield an unsaturated compound when heated at 150°.

Chlorohydroxytrimethyldihydrouracil, $C_7H_{11}O_3N_2Cl$, obtained by the action of chlorine water on trimethyluracil, crystallises from hot water, and has m. p. 154—155°.

4-*Bromo*-5-*hydroxy*-1-*phenyl*-4 : 5-*dimethyldihydrouracil*,

$$C_{12}H_{13}O_3N_2Br,$$

has m. p. 195°.

4 : 5-*Dihydroxy*-1 : 4 : 5-*trimethyldihydrouracil*, $C_7H_{12}O_4N_2$, prepared from the bromohydroxy-compound by Behrend and Grünewald's method, crystallises from water in large prisms, m. p. 165°. It reacts with boiling acetic anhydride, yielding an *acetyl* derivative, $C_9H_{14}O_5N_2$, m. p. 135—150°, and with phenyldydrazine yields a *phenylhydrazide*, $C_{13}H_{18}O_3N_4$, in the form of needles, m. p. 155—158° after sintering at 145°.

J. J. S.

Quinazolines. XXVI. Synthesis of Some Stilbazoles, Hydrazones, and Schiff Bases in the 4-Quinazolone Group. MARSTON T. BOGERT, GEORGE DENTON BELL, and CARL GUSTAVE AMEND (*J. Amer. Chem. Soc.*, 1910, 32, 1654—1664).—It has been shown in earlier papers (Bogert and Gortner, Abstr., 1909, i, 679; Bogert, Amend, and Chambers, Abstr., 1910, i, 893) that derivatives of 4-quinazolone can be easily prepared which contain a 2-methyl group and amino-groups attached to either or both the benzene and metadiazine portions of the nucleus. A study has been made of the behaviour of these different groups towards aldehydes, and the results show that with reference to their reactivity with benzaldehyde they may be arranged in the following order: (1) the 3-amino-group (in the metadiazine nucleus); (2) the 2-methyl group; and (3) the 7-amino-group (in the benzene nucleus).

When 2-methyl-4-quinazolone is boiled for ten minutes with benzaldehyde, it is converted into the stilbazole, namely, *2-styryl-4-quinazolone* (*2-styryl-4-hydroxyquinazoline*), $C_6H_4<\begin{matrix}N{=}C\cdot CH{:}CHPh \\ CO\cdot NH\end{matrix}$ or $C_6H_4<\begin{matrix}N{=\!=\!=}C\cdot CH{:}CHPh \\ C(OH){:}N\end{matrix}$, m. p. 252—253° (corr.), which forms colourless, silky needles, and yields a *bromo*-derivative. *2-o-Hydroxystyryl-4-quinazolone*, $C_6H_4<\begin{matrix}N{=}C\cdot CH{:}CH\cdot C_6H_4\cdot OH \\ CO\cdot NH\end{matrix}$, m. p. 307° (decomp.), obtained by the action of salicylaldehyde on 2-methyl-4-quinazolone, crystallises in minute, pale yellow needles, and yields bright yellow *salts* with hydrochloric acid and potassium hydroxide. *2-p-Hydroxy-m-methoxystyryl-4-quinazolone*, $C_6H_4<\begin{matrix}N{=}C\cdot CH{:}CH\cdot C_6H_3(OH)\cdot OMe \\ CO\cdot NH\end{matrix}$, m. p. 280° (corr.), forms minute, pale yellow needles and gives dark yellow alkali salts.

When 2:3-dimethyl-4-quinazolone is boiled with benzaldehyde, *2-styryl-3-methyl-4-quinazolone*, $C_6H_4<\begin{matrix}N{=}C\cdot CH{:}CHPh \\ CO\cdot NMe\end{matrix}$, m. p. 170° (corr.), is produced, which forms light yellow, slender needles.

3-Amino-2-methyl-4-quinazolone was prepared by the action of hydrazine hydrate on acetylanthranil (Bogert and Gortner, *loc. cit.*). In one experiment, a compound, m. p. 193° (corr.), was isolated, which crystallises in prisms, and is probably *acetylanthranylacetylhydrazide*, $NHAc\cdot C_6H_4\cdot CO\cdot NH\cdot NHAc$. The hydrazone, 3-benzylideneamino-2-methyl-4-quinazolone, obtained by boiling 3-amino-2-methyl-4-quinazolone (1 mol.) with benzaldehyde (1 mol.), has m. p. 187° (corr.), and not 183° as stated by Bogert and Gortner (*loc. cit.*); its *hydrochloride* softens at 220°, and decomposes without melting at about 300°. When 3-amino-2-methyl-4-quinazolone (1 mol.) is boiled with benzaldehyde (2 mols.), *3-benzylideneamino-2-styryl-4-quinazolone*,

$$C_6H_4<\begin{matrix}N{=}C\cdot CH{:}CHPh \\ CO\cdot N\cdot N{:}CHPh\end{matrix},$$

m. p. 155° (corr.), is obtained, which forms minute, nearly colourless, stellate groups of crystals; its *hydrochloride* does not melt below 300°. When this substance is treated with boiling dilute hydrochloric acid

and the product distilled with steam, benzaldehyde passes over with the distillate, and 3-*amino-2-styryl-4-quinazolone*,

$$C_6H_4<\begin{matrix}N{=}C\cdot CH{:}CHPh\\ CO\cdot N\cdot NH_2\end{matrix},$$

m. p. 164° (corr.), is obtained, which crystallises in plates or broad needles, and when heated with benzaldehyde is reconverted into its benzylidene derivative; the *benzoyl* derivative has m. p. 195° (corr.). When 3-amino-2-methyl-4-quinazolone is heated with cinnamaldehyde, salicylaldehyde, or vanillaldehyde, the methyl group is not affected, but condensation takes place only with the amino-group. 3-*Cinnamylideneamino-2-methyl-4-quinazolone*, m. p. 148—149° (corr.), forms bright yellow needles. The corresponding *salicylidene* derivative, m. p. 171° (corr.), crystallises in short, pale yellow needles, yields a bright yellow *potassium* salt and a *hydrochloride*, m. p. 250° (decomp.), and is hydrolysed by hydrochloric acid or potassium hydroxide with formation of salicylaldehyde. Although the salicylidene compound refuses to condense with a second mol. of salicylaldehyde, it condenses readily with benzaldehyde with formation of 3-*salicylideneamino-2-styryl-4-quinazolone*, $C_6H_4<\begin{matrix}N{=}C\cdot CH{:}CHPh\\ CO\cdot N\cdot N{:}CH\cdot C_6H_4\cdot OH\end{matrix}$, m. p. 232—233° (corr.), which crystallises in yellow needles. 3-*Vanillylideneamino-2-methyl-4-quinazolone*, m. p. 215—216° (corr.), forms small, yellow prisms or needles, and gives deep, yellow salts with hydrochloric acid and potassium hydroxide.

In the case of 7-amino-2-methyl-4-quinazolone, as in that of the 3-amino-derivative, condensation is possible with either the methyl or amino-group or with both. The amino-group, however, is differently situated, being in the benzene instead of the metadiazine nucleus and attached to a carbon instead of a nitrogen atom. Aldehydes condensing with the 7-amino-group should therefore yield true Schiff bases instead of hydrazones. In one experiment, a *benzylidene* derivative, m. p. 324° (corr.), was obtained, which seemed to be the Schiff base, since it was hydrolysed by potassium hydroxide with formation of benzaldehyde and the quinazolone, but this compound could not be obtained subsequently; its *acetyl* derivative has m. p. 274—276° (corr.). 7-*Acetylamino-2-styryl-4-quinazolone*,

$$NHAc\cdot C_6H_3<\begin{matrix}N{=}C\cdot CH{:}CHPh,\\ CO\cdot NH\end{matrix}$$

m. p. 323—324° (corr.), obtained by boiling 7-acetylamino-2-methyl-4-quinazolone with benzaldehyde, forms short, colourless needles.

7-Amino-2 : 3-dimethyl-4-quinazolone condenses with benzaldehyde to form 7-*amino-2-styryl-3-methyl-4-quinazolone*,

$$NH_2\cdot C_6H_3<\begin{matrix}N{=}C\cdot CH{:}CHPh\\ CO\cdot NMe\end{matrix},$$

m. p. 229·5—230° (corr.), which crystallises in yellow prisms; its *acetyl* derivative has m. p. 272° (corr.).

When 3 : 7-diamino-2-methyl-4-quinazolone is boiled with an excess of benzaldehyde, 3 : 7-*dibenzylideneamino-2-styryl-4-quinazolone*,

$$CHPh{:}N\cdot C_6H_3<\begin{matrix}N{=}C\cdot CH{:}CHPh\\ CO\cdot N\cdot N{:}CHPh\end{matrix},$$

m. p. 238° (corr.), is produced, together with small quantities of two

other *substances*, m. p. 196° (corr.) and 172° (corr.), which seem to be isomeric dibenzylidene derivatives. 7-*Acetylamino*-3-*benzylideneamino*-2-*styryl*-4-*quinazolone*, m. p. 261° (corr.), obtained by boiling 3-amino-7-acetylamino-2-methyl-4-quinazolone with excess of benzaldehyde, forms yellow needles; its solution in alcohol has a green fluorescence. 3 : 7-Diacetylamino-2-methyl-4-quinazolone condenses with benzaldehyde with formation of 3 : 7-*diacetylamino*-2-*styryl*-4-*quinazolone*, m. p. 283—284° (corr.).

3-Amino-6-acetylamino-2-methyl-4-quinazolone condenses similarly with benzaldehyde with production of 6-*acetylamino*-3-*benzylideneamino*-2-*styryl*-4-*quinazolone*, m. p. 238—239° (corr.), which forms short, silky, yellow needles. E. G.

Constitution of Indirubin. I. and II. André Wahl and P. Bagard (*Bull. Soc. chim.*, 1910, [iv], 7, 1090—1101; 1911, 9, 56—83. Compare Abstr., 1909, i, 330, 735).—I. Maillard's objection (Abstr., 1910, i, 138) to the view that the authors' new synthesis of indirubin (Abstr., 1909, i, 330) supports von Baeyer's formula for this substance is based on two main contentions: (*a*) that proof of the formation of indirubin was insufficient; (*b*) that molecular transformation may have occurred in the reaction.

In regard to (*a*) it is now shown that the synthetic indirubin, like commercial indirubin, yields Schunk and Marchlewski's colourless, crystalline compound, m. p. 204°, when reduced with zinc and acetic anhydride in presence of anhydrous sodium acetate (Abstr., 1895, i, 288). Contention (*b*) implies that both oxindole and indoxyl should condense with isatin chloride to give indirubin, but actual trial shows that when the reaction is conducted in presence of pyridine to remove the hydrogen chloride formed, indoxyl gives indigotin and no indirubin, whereas oxindole gives indirubin as chief product.

II. *m*-Bromoisatin chloride condenses with oxindole to furnish a bromoindirubin, which is isomeric with, but different from, that obtained by condensing *m*-bromoisatin with indoxylic acid. The production of isomerides in these two reactions can be explained easily from von Baeyer's, but only with difficulty from Maillard's, formula.

m-Bromoisatin chloride condenses with oxindole in benzene solution to form a *bromoindirubin*, having the formula

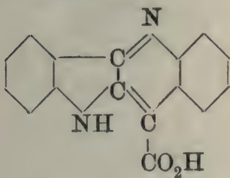
$$NH{<}{\substack{C_6H_4\\ CO}}{>}C{:}C{<}{\substack{CO\\ NH}}{>}C_6H_3Br.$$

It forms dichroic, triclinic crystals, showing oblique extinction and angle $ph' = 126°$. Its solubility is 0·192—0·199 gram in 100 grams of acetic acid at 25°. The bromoindirubin obtained by condensing *m*-bromoisatin with indoxylic acid has the formula

$$C_6H_4{<}{\substack{NH\\ CO}}{>}C{:}C{<}{\substack{C_6H_3Br\\ CO}}{>}NH,$$

and has been prepared already by von Baeyer (Abstr., 1882, 198). It forms dichroic crystals which belong to the monoclinic system, and show right extinction and angle $ph' = 101°$. Its solubility is 0·042—0·052 gram in 100 grams of acetic acid at 25°. T. A. H.

Quindoline and "Thioquindoline." EMILIO NOELTING and O. R. STEUER (*Ber.*, 1910, **43**, 3512—3517).—Indoxylic acid condenses with *o*-aminobenzaldehyde in hydrochloric acid solution, yielding quindoline (compare Fichter and Böhringer, Abstr., 1907, i, 92; Fichter and Rohner, this vol., i, 85). This is identical with indoline described by Schützenberger (this Journ., 1877, ii, 898).

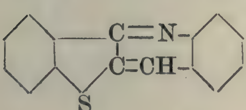


By heating indigotin with an alkaline solution of sodium thiosulphate, Geraud (Abstr., 1879, 936; 1881, 51) obtained a substance to which he assigned the formula $C_{32}H_{24}O_3N_4$. Since the same compound is also produced by the condensation of indoxyl and isatin in alkaline solution, it must be a *quindolinecarboxylic acid* of the annexed structure.

2-o-*Nitrobenzylidene-indoxyl*, $C_6H_4{<}\substack{CO-\\NH}{>}C{:}CH\cdot C_6H_4\cdot NO_2$, prepared by the condensation of *o*-nitrobenzaldehyde and indoxylic acid in aqueous acetic acid solution, crystallises in red needles, m. p. 217°; on reduction with zinc dust and acetic acid it yields quindoline.

By condensing indoxylic acid with *o*-aminobenzaldehyde in the presence of a little hydrochloric acid, 2-o-*aminobenzylidene-indoxyl*, $C_6H_4{<}\substack{CO-\\NH}{>}C{:}CH\cdot C_6H_4\cdot NH_2$, is produced; if the condensation is carried out in more acid solution, quindoline hydrochloride is obtained.

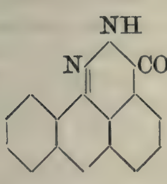
3-*Keto*-2-o-*nitrobenzylidene-thionaphthen*, $C_6H_4{<}\substack{CO\\S-}{>}C{:}CH\cdot C_6H_4\cdot NO_2$, prepared from *o*-nitrobenzaldehyde and 3-hydroxythionaphthen-2-carboxylic acid in acetic acid solution, crystallises from alcohol in orange-yellow needles, m. p. 171°; on reduction it yields "*thioquindoline*" (annexed formula).



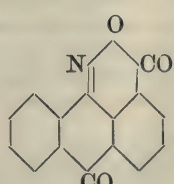
The latter crystallises in almost colourless needles, m. p. 169°, and with concentrated acids forms yellow salts, which are decomposed by water; the *hydrochloride* and *picrate* are described.

Quindoline and "thioquindoline" dye tannin-mordanted wool, silk, and cotton pale yellow; with quindolinecarboxylic acid the shade is somewhat deeper. F. B.

Anthraquinone-1-carboxylic Acid. FRITZ ULLMANN and WILLEM VAN DER SCHALK (*Ber.*, 1911, **44**, 128—129).—*Anhydro-anthraquinone*-9-*hydrazone*-1-*carboxylic acid* (*pyridazonanthrone*) (I), obtained by the action of hydrazine hydrate on the chloride of anthraquinone-1-carboxylic acid, crystallises in needles which are sparingly soluble in the usual solvents, but dissolve in sodium hydroxide to orange-yellow solutions. Phenylhydrazine gives the corresponding *N*-phenylpyridazonanthrone. Anthraquinone-1-carb-



(I.)



(II.)

oxylic acid reacts readily with hydroxylamine in the presence of sodium acetate solution, yielding *oxazonanthrone* (II) in the form of pale yellow needles, m. p. 247°. J. J. S.

Method for Preparing Aromatic Acylguanidines. PAUL PIERRON (*Compt. rend.*, 1910, 151, 1364—1366. Compare Wheeler and Johnson, Abstr., 1902, i, 27).—Aromatic acylguanidines are best prepared by boiling the aromatic acylcyanamides with the hydrochloride of an aromatic amine in alcoholic solution; thus benzoylcyanamide and aniline hydrochloride yield benzoylphenylguanidine, the *hydrochloride* of which has m. p. 159°. *Benzoyl*-m-*tolylguanidine*, C_7H_8·NH·C(NHBz):NH, crystallises in needles or leaflets, m. p. 71°; the *hydrochloride* has m. p. 170°. *Cinnamoylphenylguanidine*,

CHPh:CH·CO·NH·C(NHPh):NH,

forms prismatic needles, m. p. 140°; *benzoyl-ψ-cumidylguanidine*, $C_{17}H_{19}ON_3$, occurs in prismatic needles, m. p. 140—141°.

On boiling acylcyanamides with *o*-phenylenediamine in alcoholic solution, an acylaminobenziminazole is produced. The arylcyanamides do not readily undergo this condensation. *Cinnamoyl*-o-*phenyleneguanidine* [2-*cinnamoyliminobenziminazole*],

$$C_6H_4{<}^{NH}_{NH}{>}C{:}N{\cdot}CO{\cdot}CH{:}CHPh,$$

crystallises in needles, m. p. 262°. W. O. W.

Pechmann's Isomeric Hydrazidines. HENRY L. WHEELER and TREAT B. JOHNSON (*Ber.*, 1911, 44, 151).—The authors have already shown (Abstr., 1904, i, 628) that the formulæ suggested by Busch and Ruppenthal (this vol., i, 86) for Pechmann's hydrazidines (Abstr., 1896, i, 31), namely, NH_2·NPh·CPh:NPh and NHPh·NH·CPh:NPh, are correct. J. J. S.

Preparation of 4-*iso*Valerylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone and of 4-α-Bromo*iso*valerylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone. KNOLL & Co. (D.R.-P. 227013).—Compounds possessing valuable therapeutic properties are obtained by introducing *iso*valeryl or substituted *iso*valeryl residues into 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone.

4-iso*Valerylamino*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone*, m. p. 203°, odourless and with a bitter taste, is prepared by heating 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone with *iso*valeric acid and phosphorus trichloride at 125° during half an hour, treating with sodium carbonate, and crystallising the dried product from benzene; its aqueous solutions give a blood-red coloration with ferric chloride.

4-α-*Bromo*iso*valerylamino*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* is obtained when α-bromo*iso*valeryl bromide is substituted for the *iso*valeric acid and phosphorus trichloride in the foregoing preparation; it forms glistening, colourless needles, m. p. 206° (decomp.), is odourless, but has a bitter taste, and forms crystalline *salts* with acids and a yellow coloration with ferric chloride. F. M. G. M.

Preparation of 4-Imino-5-oximino-2 : 6-diketopyrimidine and its 3-Alkyl Derivative. EMANUEL MERCK (D.R.-P. 227390).—The action of nitrous acid on a hot dilute acetic acid solution of cyano-

acetylmethylcarbamide, NHMe·CO·NH·CO·CH_2·CN, yields *oximinocyanoacetylmethylcarbamide*, NHMe·CO·NH·CO·C(:NOH)·CN, colourless crystals, m. p. 218° (decomp.). When this substance is warmed with 30% sodium hydroxide (4 parts), an orange-yellow precipitate slowly separates, which on the addition of acetic acid is converted into the characteristic red crystals of 4-imino-5-oximino-2 : 6-diketo-3-methylpyrimidine, $NH<\begin{matrix}CO\cdot C(:NOH)\\ CO\text{——}NMe\end{matrix}>C:NH$. Analogous results are obtained when cyanoacetylcarbamide is employed in the foregoing reaction; a yellow, crystalline *sodium* derivative separates on treatment with sodium nitrite, yielding on acidification *oximinocyanoacetylcarbamide*, glistening, colourless crystals, m. p. 220°, which are readily converted into the corresponding 4-imino-5-oximino-2 : 6-diketopyrimidine. The sodium hydroxide can in this reaction be replaced by sodamide, sodium ethoxide, or an alkylcarbamide. F. M. G. M.

Preparation of Anthrapyrimidines and Anthrapyrimidones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 225982).—The reaction between aminoanthraquinones and acid amides has been previously described (Abstr., 1910, i, 445); the same result is now obtained with acylaminoanthraquinones and ammonia, 1-anthrapyrimidone (*loc. cit.*) having been prepared by heating aminoanthraquinoneurethane with ammonium hydroxide at 150°; likewise, 1 : 4-diaminoanthraquinonemonourethane yields 4-*amino*-1-*anthrapyrimidone*, brown crystals, and 2-*bromo*-4-*amino*-1-*μ*-*methylanthrapyrimidine*, a brown powder, is obtained from 2 : 4-dibromo-1-acetylaminoanthraquinone.

A tabulated description of the following compounds, with the colours of their solutions in various solvents, is given in the original: 1-*aminoanthraquinoneurethane*, greenish-yellow crystals; 1-*aminoanthraquinonecarbamide chloride*, orange crystals; 1 : 4-*diaminoanthraquinonemonourethane*, garnet-red crystals; 4-*chloro*-1-*aminoanthraquinoneurethane*, golden-yellow crystals; 2 : 4-*dibromo*-1-*acetylaminoanthraquinone*, brownish-yellow crystals; 4-*amino*-1-*anthrapyrimidone*, dark brown crystals. F. M. G. M.

4-Dibromo-1 : 2 : 3-triazol-5-one-1-acetamide. THEODOR CURTIUS and ERNST WELDE (*Ber.*, 1910, 43, 857—862).—The dibromo-derivative mentioned previously (Abstr., 1907, i, 450) is shown to be 4-*dibromo*-1 : 2 : 3-*triazole*-5-*one*-1-*acetamide*,

$$\begin{matrix}N\text{===}N\\ |\quad\quad\\ CBr_2\cdot CO\end{matrix}>N\cdot CH_2\cdot CO\cdot NH_2.$$

Its formation from the ammonium salt of 5-hydroxy-1 : 2 : 3-triazole-1-acetamide is represented by means of the equation:

$$\begin{matrix}N\text{=====}N\\ |\quad\quad\quad\\ CH:C(O\cdot NH_4)\end{matrix}>C\cdot CH_2\cdot CO\cdot NH_2 + 2Br_2 =$$
$$C_4H_4O_2N_4Br_2 + HBr + NH_4Br,$$

and its formation from the nitroso-derivative by the equation:

$$C_4H_8O_3N_5 + 2Br_2 = C_4H_4O_2N_4Br_2 + NOBr + NH_4Br,$$

the nitrosyl bromide formed immediately yielding nitrous and hydrobromic acids.

The dibromo-derivative crystallises from hot alcohol in colourless, glistening needles, m. p. 151° (decomp.), after turning brown at 120°. It changes colour when exposed to the air for several hours, and then has an odour of bromine. When boiled with dilute sulphuric acid, it is hydrolysed to nitrogen, ammonia, glycine, and dibromoglycollic acid, the last of which is further hydrolysed to hydrobromic and oxalic acids. The same decomposition occurs, only more slowly, when the bromo-derivative is boiled with water. J. J. S.

Derivatives of *iso*Uric Acid. HEINRICH BILTZ (*Ber.*, 1910, **43**, 3553—3562).—It has been shown (Abstr., 1909, i, 740) that diethoxy-4 : 5-diphenyldihydroglyoxalone is converted on heating at the m. p. into 5-ethoxy-4 : 5-diphenyl*iso*glyoxalone. Diethoxy-1 : 3 : 7-trimethyluric acid might be expected to behave similarly, but it does not change at the m. p. However, on boiling it in glacial acetic acid solution, *5-ethoxy-trimethyl*iso*uric acid*, $\begin{array}{l}\mathrm{NMe{\cdot}CO{\cdot}C(OEt)} \\ \mathrm{CO{\cdot}NMe{\cdot}C{:}N{\cdot}CO}\end{array}\!\!>\!\mathrm{NMe}$, is formed. This can be crystallised from cold alcohol without change, but on boiling with alcohol containing a little acid, the diethoxy-derivative is regenerated. On reduction with zinc and acetic acid, hydrogen is added at positions 4 and 9, that in 4 is immediately eliminated with the ethoxyl group in position 5, and trimethyluric acid is obtained.

5-Ethoxytrimethyl*iso*uric acid is completely analogous to 5-ethoxydiphenyl*iso*glyoxalone, and the conclusion is drawn that the ethoxyl group in position 4 and the imino-hydrogen in position 9 are on opposite sides of the plane of the glyoxalone ring.

By the action of chlorine on trimethyluric acid in chloroform solution, a dichloride is first formed soluble in chloroform, chlorine being added in positions 4 and 5. This is unstable, hydrogen chloride being eliminated between positions 4 and 9, and a chlorine derivative of *iso*uric acid is obtained,

$$\begin{array}{l}\mathrm{NMe{\cdot}CO{\cdot}CCl{\cdot}NMe} \\ \mathrm{CO{\cdot}NMe{\cdot}CCl{-}NH}\end{array}\!\!>\!\mathrm{CO} \longrightarrow \begin{array}{l}\mathrm{NMe{\cdot}CO{\cdot}CCl{\cdot}NMe} \\ \mathrm{CO{\cdot}NMe{\cdot}C{=\!=}N}\end{array}\!\!>\!\mathrm{CO}.$$

Alcohol converts this chloride into 5-ethoxy-1 : 3 : 7-trimethyl*iso*uric acid; water readily converts it into *apo*caffeine.

*5-Ethoxy-*1 : 3 : 7*-trimethyl*iso*uric acid* forms long, thin, colourless needles, m. p. 174—176°.

*5-Methoxy-*1 : 3 : 7*-trimethyl*iso*uric acid* crystallises in obliquely cut, six-sided, columnar forms, m. p. 205°.

*5-Chloro-*1 : 3 : 7*-trimethyl*iso*uric acid* separates in colourless, flat needles or prisms with oblique end faces and a rectangular cross section, m. p. 158° (decomp.). The corresponding 5-bromo-compound could not be obtained. E. F. A.

Hydroxyazo-compounds and Ketohydrazones. I.—III. KARL AUWERS [and, in part, HUGO DANNEHL and A. BOENNECKE] (*Annalen*, 1910, **378**, 210—260. Compare Auwers, Abstr., 1908, i, 477).—The results of previous investigations indicate that when possible the phenylhydrazones of benzoquinones and naphthaquinones undergo

molecular rearrangement into azo-compounds, whereas with mixed azo-derivatives the reverse process takes place.

Phenanthraquinonephenylhydrazone (Zincke, Abstr., 1883, 1135; Werner, *Annalen*, 1902, **321**, 304), when benzoylated in the presence of pyridine, yields a benzoyl derivative which is identical with the product obtained by condensing phenanthraquinone with *as*-benzoylphenylhydrazine in the presence of mineral acids. From the readiness with which it is hydrolysed and from the fact that when reduced with zinc dust and cold acetic acid the chief products are aniline and 9-benzoylamino-10-hydroxyphenanthrene (87% yield), the conclusion is drawn that the benzoyl compound is an *O*-derivative:

$$\begin{array}{l} C_6H_4\cdot C\cdot N\colon NPh \\ \mid \qquad\;\; \| \\ C_6H_4\cdot C\cdot OBz \end{array} \longrightarrow \begin{array}{l} C_6H_4\cdot C\cdot NHBz \\ \mid \qquad\;\; \| \\ C_6H_4\cdot C\cdot OH \end{array} + NH_2Ph.$$

In the condensation of phenanthraquinone with benzoylphenylhydrazine, a wandering of the benzoyl group from nitrogen to oxygen occurs, a wandering analogous to that observed in the condensation of β-naphthaquinone with benzoylphenylhydrazine. The same *O*-acetyl derivative is obtained by acetylating phenanthraquinonephenylhydrazone and by condensing phenanthraquinone with *as*-acetylphenylhydrazine. This acetyl derivative is so readily hydrolysed that it is difficult to purify. The general conclusion drawn is that phenanthraquinonephenylhydrazone is 9-benzeneazo-10-phenanthrol.

9-*Benzeneazo*-10-*phenanthryl benzoate*, $C_{27}H_{18}O_2N_2$, crystallises from glacial acetic acid in glistening, red plates, m. p. 193—194°. 9-*Benzoylamino*-10-*phenanthrol*, $C_{21}H_{15}O_2N$, crystallises from glacial acetic acid in glistening, flat needles, m. p. 248—249°. 9-*Benzeneazo*-10-*phenanthryl acetate*, $C_{22}H_{16}O_2N_2$, crystallises from light petroleum in brilliant red plates, m. p. 139—140°, and is hydrolysed when warmed with alcohol or acetic acid.

The question as to the constitution of Knorr's 4-benzeneazo-5-keto-1-phenyl-3-methylpyrazolone has been investigated (Knorr, Abstr., 1887, 678; 1888, 724; Japp and Klingemann, Trans., 1888, **53**, 519; Wedekind, *Annalen*, 1897, **295**, 330; Bülow, Abstr., 1899, i, 355; Eibner, Abstr., 1903, i, 871). The same benzoyl derivative is obtained by: (1) the action of benzoyl chloride on the sodium derivative suspended in dry ether; (2) the action of benzoyl chloride and sodium hydroxide solution on an aqueous acetone solution of the pyrazolone; (3) the condensation of ketophenylmethylpyrazolone with *as*-phenylbenzoylhydrazine hydrochloride in dilute alcohol. It is regarded as the *O*-benzoyl derivative, $N{<}\begin{array}{l} CMe\cdot C\cdot N\colon NPh \\ \qquad\quad\;\| \\ NPh\cdot C\cdot OBz \end{array}$, since when reduced with zinc dust and cold acetic acid it yields appreciable amounts of aniline, together with benzanilide and rubazonic acid.

$$R{<}\begin{array}{l} C\cdot N\colon NPh \\ \| \\ C\cdot OBr \end{array} \begin{array}{l} \longrightarrow R{<}\begin{array}{l} C\cdot NH_2 \\ \| \\ C\cdot OH \end{array} + NHPhBz. \\ \\ \longrightarrow R{<}\begin{array}{l} C\cdot NHBz \\ \| \\ C\cdot OH \end{array} + NH_2Ph. \end{array}$$

It has not been found possible to isolate the *N*-benzoyl derivative of the aminohydroxyphenylmethylpyrazole.

Knorr's compound is thus a true azo-derivative, and as it dissolves readily in alkalis, it is represented by the enolic formula

$$\mathrm{N}{<}\begin{array}{l}\mathrm{CMe{\cdot}C{\cdot}N{:}NPh}\\ \mathrm{NPh{\cdot}C{\cdot}OH}\end{array},$$

and is 4-benzeneazo-5-hydroxy-1-phenyl-3-methylpyrazole.

When the β-phenylhydrazone of $\alpha\beta$-diketobutyric acid is condensed with benzoylphenylhydrazine, water is eliminated, and Knorr's azo-compound and ethyl benzoate are obtained, instead of the expected *N*-benzoyl derivative, $\mathrm{N}{<}\begin{array}{l}\mathrm{CMe{\cdot}C{:}N{\cdot}NPhBz}\\ \mathrm{NPh{\cdot}CO}\end{array}$. The free hydroxypyrazole is also formed (1) when the benzoylated osazone of the diketobutyric acid is warmed with benzene and phosphoric oxide; (2) when the β-phenylhydrazone of ethyl $\alpha\beta$-diketobutyrate is condensed with *as*-benzoylphenylhydrazine hydrochloride in alcoholic solution, both with and without the addition of sodium acetate, and (3) when the dibenzoyl derivative of the osazone of the ethyl diketobutyrate is warmed with alcoholic potassium hydroxide.

The methyl derivative obtained by condensing ketophenylmethylpyrazolone with *as*-phenylmethylhydrazine must be the *N*-methyl ether, $\mathrm{N}{<}\begin{array}{l}\mathrm{CMe{\cdot}C{:}N{\cdot}NMePh}\\ \mathrm{NPh{\cdot}C{:}O}\end{array}$, as alkyl groups do not wander under these conditions. This constitution is confirmed by the fact that when reduced with zinc and acetic acid, methylaniline is obtained, but no trace of aniline. The same methyl ether, together with a small amount of the isomeric *O*-methyl ether, $\mathrm{N}{<}\begin{array}{l}\mathrm{CMe{\cdot}C{\cdot}N{:}NPh}\\ \mathrm{NPh{\cdot}C{\cdot}OMe}\end{array}$, is formed when Knorr's azo-compound is methylated by means of methyl iodide or sulphate and alkali. When reduced, the *O*-methyl ether yields appreciable amounts of aniline.

The *N*-methyl ether is readily hydrolysed to the monomethyl derivative of ethyl diketobutyrate osazone, whereas the *O*-ether is not acted upon when boiled with alcoholic potassium hydroxide.

The *benzoyl* derivative of 4-benzeneazo-5-hydroxy-1-phenyl-3-methylpyrazole, $C_{23}H_{18}O_2N_4$, crystallises from alcohol in long, yellow, glistening needles, or from light petroleum in quadratic plates, m. p. 137°, which are readily hydrolysed when boiled with 50% acetic acid.

The *dibenzoyl* derivative of 4-*amino*-5-*hydroxy*-1-*phenyl*-3-*methylpyrazole*, $\mathrm{N}{<}\begin{array}{l}\mathrm{CMe{\cdot}C{\cdot}NHBz}\\ \mathrm{NPh{\cdot}C{\cdot}OBz}\end{array}$, prepared by benzoylating the corresponding amine, crystallises from dilute alcohol in colourless, glistening needles, m. p. 196°, and on hydrolysis yields a colourless compound, m. p. 110—115°, probably the acid $\mathrm{NHPh{\cdot}N{:}CMe{\cdot}CH(NHBz){\cdot}CO_2H}$, which, when heated, yields the N-*benzoyl* derivative, $\mathrm{N}{<}\begin{array}{l}\mathrm{CMe{\cdot}CH{\cdot}NHBz}\\ \mathrm{NPh{\cdot}CO}\end{array}$, m. p. 183°. Keto-1-phenyl-3-methylpyrazolone, prepared by Sachs and Barschall's method (Abstr., 1902, i, 504), has m. p. 121°. The *monobenzoylosazone* of $\alpha\beta$-diketobutyric acid,

$$\mathrm{NHPh{\cdot}N{:}CMe{\cdot}C(CO_2H){:}N{\cdot}NBzPh},$$

crystallises from light petroleum in slender, pale yellow needles, m. p.

110—111°, and dissolves in cold sodium hydroxide solution without undergoing hydrolysis. Ethyl $\alpha\beta$-diketobutyrate and benzoylphenylhydrazine yield the *dibenzoylated osazone*, $C_{32}H_{28}O_4N_4$, even in the presence of an excess of ester. It crystallises from dilute methyl alcohol in long, colourless prisms, m. p. 190°. Ethyl $\alpha\beta$-diketobutyrate and phenylmethylhydrazine yield the *dimethylosazone*,

$$NMePh\cdot N:CMe\cdot C(CO_2Et):N\cdot NMePh,$$

which crystallises from alcohol in pale yellow, glistening prisms, m. p. 103—104°. The *phenylmethylhydrazone* of 4-keto-1-phenyl-3-methyl-5-pyrazolone, $C_{17}H_{16}ON_4$, crystallises from dilute alcohol in glistening, orange-yellow, felted needles, m. p. 144°, and is insoluble in alkalis; the isomeric O-*methyl ether* forms compact, yellow prisms, m. p. 78°.

It has not been found possible to acetylate or benzoylate Graebe and Gfeller's acenaphthenequinonephenylhydrazone (Abstr., 1893, i, 657), but the *benzoyl* derivative, $C_{25}H_{16}O_2N_2$, can be prepared by condensing the quinone with benzoylphenylhydrazine hydrochloride and alcohol. It crystallises in glistening, orange-red needles, m. p. 170°, and is readily hydrolysed by cold alcoholic sodium hydroxide. When reduced with zinc and acetic acid, it yields no trace of aniline, and is therefore a *N*-benzoyl derivative, and the phenylhydrazone probably has the hydrazone and not the azo-structure.

Acenaphthenequinonephenylmethylhydrazone, $C_{19}H_{14}ON_2$, crystallises from acetone in dark red needles, m. p. 114°, and, when reduced, yields methylaniline and no trace of aniline.

Camphorquinonephenylhydrazone cannot be directly acylated, but the *benzoyl* derivative, $C_{23}H_{24}O_2N_2$, can be obtained, by condensing the quinone with benzoylphenylhydrazine, in the form of colourless, felted needles, m. p. 153°. This is also a *N*-benzoyl derivative, and the parent substance a hydrazone, which exists in one form only (compare Lapworth and Hann, Trans., 1902, **81**, 1514).

The two *N*-benzoyl derivatives, unlike most other *N*-benzoylated compounds, are readily hydrolysed. The following new *N*-benzoyl derivatives, prepared by condensing the ketones with benzoylphenylhydrazine, are not readily hydrolysed by alkalis: *Ethyl acetoacetate benzoylphenylhydrazone*, $C_{19}H_{20}O_3N_2$, forms compact, colourless, quadratic crystals, m. p. 144—145°, and with alcoholic potash yields the *benzoylphenylhydrazone* of acetoacetic acid, $C_{17}H_{16}O_3N_2$, in the form of small, colourless prisms, m. p. 203°.

Diacetyldibenzoylosazone, $C_{30}H_{26}O_2N_4$, crystallises from boiling glacial acetic acid in slender needles, m. p. 249°, and is formed even at $-15°$ in the presence of an excess of the ketone. *Benzil-benzoylphenylhydrazone*, $C_{27}H_{20}O_2N_2$, crystallises from light petroleum in slender, prismatic needles, m. p. 176°.

Baeyer and Claisen's phenylazoacetylacetone (Abstr., 1888, 828) is best prepared by the gradual addition of a solution of phenyldiazonium chloride exactly neutralised with sodium carbonate to a cold solution of acetylacetone (1 mol.) in sodium carbonate (0·5 mol.). The benzoyl derivative (Pechmann, Abstr., 1893, i, 84) is most readily prepared by the Schotten-Baumann method; it has m. p. 160—161°, is readily hydrolysed by alkalis, and is sometimes accompanied by an *isomeride*, m. p. 134°. When reduced, the benzoyl

derivative yields benzanilide, but no trace of aniline. The compound is thus a *N*-benzoyl derivative, and the parent substance a γ-phenylhydrazone of $\beta\gamma\delta$-triketopentane and not an azo-derivative.

Benzoylacetylacetone, in the form of its sodium derivative, reacts with a neutralised solution of phenyldiazonium chloride, yielding O-*benzeneazodiacetylbenzoylmethane*, NPh:N·O·CMe:CBzAc, which crystallises from methyl alcohol in golden-yellow, prismatic needles, m. p. 77—78°. The compound is not affected when boiled with alcohol; with cold alkalis, or with an ethereal solution of hydrogen chloride, it yields the phenylhydrazone of phenyl methyl triketone, and when boiled with glacial acetic acid yields benzoylacetone. The reaction with hydrogen chloride is similar to that described by Dimroth and Hartmann as characteristic of *O*-azo-compounds (Abstr., 1909, i, 66). The azo-compound (m. p. 77—78°) reacts with an alcoholic solution of β-naphthol, yielding benzeneazo-β-naphthol and benzoylacetylacetone. When reduced with zinc dust and acetic acid, the azo-compound yields appreciable amounts of aniline. The isomeric *acetylphenylhydrazone* of phenyl methyl triketone,

CAcBz:N·NAcPh,

is formed when the *O*-azo-compound is boiled for four hours with toluene; it separates from alcohol in colourless crystals, m. p. 158°, and when reduced yields acetanilide, but no trace of aniline. The compound is isomeric with the benzoyl derivative of phenylazoacetylacetone, m. p. 160°.

These results agree with Pechmann's view that the compounds derived from diazo-compounds and aliphatic ketones with the reactive $\cdot CO \cdot CH_2 \cdot$ group are not azo-compounds, but hydrazones.

Generalisations based on the constitution of *N*-benzoyl derivatives and the readiness with which they are hydrolysed cannot be drawn.

J. J. S.

Method for Determining the Individuality or Plurality of Diastases in a Liquid. PIERRE ACHALME and BRESSON (*Compt. rend.*, 1910, 151, 1369—1372).—In order to ascertain whether a particular liquid contains one or more enzymes, the authors suggest that it should be allowed to act, under identical conditions, on solutions of two different substances capable of being hydrolysed by it, and on a solution containing a mixture of the same two substances. If two diastases are present, the action on the mixture should be the sum of the action on the two substances taken individually, whilst if only one enzyme is present, the action on the mixture should not exceed that on either substance alone. The results of illustrative experiments are given in tabular form. It is found that the time taken to effect hydrolysis in the three solutions is the same if two diastases are present, but that when only one enzyme is acting, a longer period is required to hydrolyse the mixture. W. O. W.

Chlorophyll. XI. Chlorophyllase. RICHARD WILLSTÄTTER and ARTHUR STOLL (*Annalen*, 1910, 378, 18—72).—See this vol., i, 141.

Organic Chemistry.

Synthesis of *as*-Heptachloropropane from Tetrachloroethylene and Chloroform with the Co-operation of Aluminium Chloride. JACOB BÖESEKEN and H. J. PRINS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 685—687).—It has previously been shown (Abstr., 1910, i, 152) that when dichloroacetyl chloride is decomposed by aluminium chloride, one of the products is a crystalline substance, m. p. 32°, to which the composition C_5Cl_{10} was assigned. A larger quantity of this substance has now been prepared, and it is found to be identical with the *as*-heptachloropropane obtained by Fritsch from pentachloroacetone and phosphorus pentachloride (Abstr., 1898, i, 63). The heptachloropropane may also be prepared by the direct addition of chloroform to tetrachloroethylene under the influence of aluminium chloride.

This synthesis gives another proof that the theory of the formation of intermediate products as an explanation of Friedel and Crafts' reaction must be abandoned, as there are no indications of the formation of such products. It may be assumed that aluminium chloride renders the chloroform active, so that the molecular parts $CHCl_2$ and Cl attach themselves to the double linking of the ethylene perchloride, also rendered active.

It is also shown that pentachloroethane yields *as*-heptachloropropane with chloroform and aluminium chloride. N. C.

Preparation of Bromides from Primary and Secondary Saturated Alcohols. FELIX TABOURY (*Bull. Soc. chim.*, 1911, [iv], **9**, 124—125).—Fournier (Abstr., 1906, i, 787) has shown that hydrogen bromide reacts with primary and secondary saturated alcohols at the ordinary pressure, giving good yields of alkyl bromides. The author states that it is unnecessary to prepare the hydrogen bromide separately, and gives details for carrying out the reaction in one large flask. Yields varying from 75 to 85% of methyl, ethyl, propyl, and *iso*propyl bromides were obtained in this way. In the case of *iso*butyl bromide the yield fell to 50%, owing to a secondary action of the bromine on the bromide produced. It was found in this case that on raising the temperature at the end of the experiment, a liquid was obtained, b. p. 149—150°; this is dibromo*iso*butane, $CH_2Br\cdot CMe_2Br$. N. C.

Acetylenic Pinacone [$\beta\epsilon$-Dimethyl-Δ^γ-hexinene-$\beta\epsilon$-diol]. GEORGES DUPONT (*Compt. rend.*, 1911, **152**, 197—199).—$\beta\epsilon$-Dimethyl-Δ^γ-hexinene-$\beta\epsilon$-diol, $OH\cdot CMe_2\cdot C\vdots C\cdot CMe_2\cdot OH$ (Jotsitch, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1545) is a colourless substance, m. p. 95°, which, unlike corresponding saturated compounds, does not form a hydrate. It resembles these subtances, however, in its behaviour towards the halogen acids, but approaches more closely to $\beta\delta$-dimethylpentane-

$\beta\delta$-diol (Franke, Abstr., 1905, i, 111; 1907, i, 816) in its reactions with dehydrating agents.

The corresponding *dibromide*, $CMe_2Br\cdot C\vdots C\cdot CMe_2Br$, m. p. 39°, b. p. 219°, is an exceedingly stable substance. In its formation by the action of hydrogen bromide, an unstable intermediate compound was noticed, m. p. about 50°. The corresponding *dichloride* has m. p. 29°, b. p. 62—63°/15 mm.

By the action of dilute sulphuric acid on the diol, the two following substances are obtained in proportions varying with the concentration and duration of heating. (1) *β-Methyl-ϵ-methylene-Δ^γ-hexinene-β-ol*, $CH_2\colon CMe\cdot C\vdots C\cdot CMe_2\cdot OH$, a pale yellow liquid with an agreeable odour, m. p. −2°, b. p. 159—160°, D^{15} 0·8772, n_D 1·4687. When treated with hydrogen in presence of spongy platinum it yields dimethyl*iso*amylcarbinol (Konowaloff, Abstr., 1902, i, 336). (2) *$\beta\epsilon$-Dimethylene-Δ^γ-hexinene*, $CH_2\colon CMe\cdot C\vdots C\cdot CMe\colon CH_2$, is a colourless, mobile liquid, b. p. 123—124°, D^{15} 0·7898, n_D 1·4859, which rapidly becomes resinous on exposure to air. It is best prepared by the action of potassium hydroxide on the foregoing dibromide. On reduction it yields $\beta\epsilon$-dimethylhexane. W. O. W.

Existence of Chlorosulphinic Esters. ARTHUR STÄHLER and ERIK SCHIRM (*Ber.*, 1911, 44, 319—323).—Well-cooled ethyl alcohol is treated slowly with thionyl chloride, and the mixture is distilled under 19 mm. pressure after being kept overnight. The resulting ethyl chlorosulphinate, $Cl\cdot SO_2Et$, b. p. 29°/13 mm., is a faintly yellow liquid, which decomposes at its b. p., 122°, under ordinary pressure into sulphur dioxide and ethyl chloride, as found by previous investigators. The methyl ester, b. p. 19°/13 mm. or 102°/755 mm. (decomp.), is obtained, and behaves in a similar manner. Neither of the esters, however, can be separated completely from the excess of the thionyl chloride on account of proximity of b. p. The *propyl* ester, however, has been obtained in a pure state as a colourless liquid, b. p. 78°/75 mm. The iso*butyl* ester has b. p. 48·5°/9 mm.

The chlorosulphinic esters are very unstable substances, which are vigorously decomposed by water into sulphur dioxide, hydrogen chloride, and an alcohol. C. S.

Delepine's Phosphorescent Esters. JAIME FERRER HERNÁNDEZ and ANGEL DEL CAMPO Y CERDAN (*Anal. Fis. Quim.*, 1911, 9, 17—26. Compare Delepine, Abstr., 1910, i, 295, 545).—The authors have repeated Delepine's observations on the phosphorescence of dimethyl dithiocarbonate, $OMe\cdot CS\cdot SMe$, and find that ionisation of the air is produced during the phenomenon, whilst the compound appears to possess feeble radioactivity. The potassium methyl salt, $OMe\cdot CS\cdot SK$ yields methyl tetrathionate when oxidised by potassium permanganate or sodium perborate in dilute acid solution. G. D. L.

Separation of the Liquid Fatty Acids (Unsaturated) from the Solid Fatty Acids (Saturated) in Natural Mixtures of Fatty Acids, and the Ammonium Salts of Some Fatty Acids. II. PIETRO FALCIOLA (*Gazzetta*, 1910, 40, ii, 425—435. Compare this vol., i, 5).—When applied to mixtures of natural origin

the method previously described does not effect a rigorously quantitative separation, but nevertheless it may be employed with more or less success, and yields more satisfactory results in the case of mixtures containing a preponderance of the solid acids. The ammonium salts of the solid fatty acids (such as the palmitate and stearate) are more soluble in ammoniacal alcohol containing ammonium salts of liquid fatty acids (for example, the oleate) than in that solvent alone. Moreover, the solid fatty acids separated by the method always contain appreciable quantities of the liquid fatty acids.

Ammonium linoleate, $C_{17}H_{31}\cdot CO_2\cdot NH_4$, is prepared by passing dry ammonia into a cold ethereal salution of the acid in an atmosphere of hydrogen. In presence of ammonia and lime, the pasty mass obtained becomes solid. It begins to melt at 57—58°, and is completely melted at 75°, forming a red liquid. *Ammonium erucate*,

$$C_{22}H_{41}O_2\cdot NH_4,$$

is similarly prepared, and has m. p. 70—77°. *Ammonium laurate*, $C_{11}H_{23}\cdot CO_2\cdot NH_4$, is a white substance, m. p. about 75°. *Ammonium myristate*, $C_{13}H_{27}\cdot CO_2\cdot NH_4$, has m. p. about 75—90°. *Ammonium octoate*, $C_8H_{15}O_2\cdot NH_4$, has m. p. 70—85°. Ammonium hexoate may be prepared in the same way. *Ammonium crotonate*, $C_3H_4\cdot CO_2\cdot NH_4$, forms colourless crystals, m. p. 105—115°. *Ammonium butyrate*, $C_3H_7\cdot CO_2\cdot NH_4$, has m. p. 70—85°. R. V. S.

Linolenic Acid and Linseed Oil. ADOLF ROLLETT (*Zeitsch. physiol. Chem.*, 1911, **70**, 404—407).—Polemical (compare Erdmann and Bedford, Abstr., 1910, i, 810; Rollet, Abstr., 1909, i, 760). Pure linolenic acid has the iodine value 273·7. E. F. A.

Action of the Chlorides of α-Alkyloxy-acids on Organometallic Derivatives of Zinc. EDMOND É. BLAISE and L. PICARD (*Compt. rend.*, 1911, **152**, 268—269).—The chlorides of α-alkyloxy-acids are acted on abnormally by organozinc iodides, giving rise under some conditions to an ether, in addition to the usual alkyloxy-ketone. This arises from the elimination of carbon monoxide from the acid chloride, probably through catalytic influence of the zinc compound. The action is represented as: $R\cdot O\cdot CH_2\cdot COCl = R\cdot O\cdot CH_2Cl + CO$; $R\cdot O\cdot CH_2Cl + ZnR'I = ZnClI + R\cdot O\cdot CH_2R'$. The yield of ether increases and that of ketone diminishes as the temperature of reaction rises. The proportion of ether increases also with the molecular weight of the zinc salt; thus, from zinc *n*-heptyl iodide only ethyl octyl ether was obtained. When R or R′ are cyclic, only the ketone is formed; thus ethoxyacetyl chloride and zinc *p*-tolyl bromide gave p-*tolyl ethoxymethyl ketone*, $OEt\cdot CH_2\cdot CO\cdot C_7H_7$, b. p. 135°/9·5 mm.; the *oxime* has m. p. 57°, and the p-*nitrophenylhydrazone*, m. p. 80°. The yield of ketone increases also with the weight of R. *iso*Butoxyacetyl chloride and zinc ethyl iodide gave *n*-propyl *iso*butyl ether (10%) and *ethyl* iso*butoxymethyl ketone* (50%), b. p. 68—69°/13 mm.; *oxime*, b. p. 116—117°/14 mm.; *semicarbazone*, m. p. 72°. Phenoxyacetyl chloride gave only *phenoxymethyl ethyl ketone*, b. p. 129°/14 mm.; *semicarbazone*, m. p. 102°; p-*nitrophenylhydrazone*, prisms, m. p. 153°.

W. O. W.

The Preparation of β-Alkyloxy-compounds. M. H. PALOMAA and SULO KILPI (*Chem. Zentr.*, 1910, ii, 1453; from *Ann. Finn. Akad. Wiss.*, *A* **2**, No. 3).—The preparation of the esters of hydracrylic acid by the action of sodium alkyloxides on ethyl β-chloropropionate gave unsatisfactory results; the action was better in the case of the β-iodopropionate. *Methyl β-methoxypropionate*,

$$OMe\cdot CH_2\cdot CH_2\cdot CO_2Me,$$

is a colourless liquid, b. p. 143·4—143·6°/750 mm., D_{15}^{15} 1·0148. *Ethyl β-ethoxypropionate* has b. p. 49·5—49·8°/7 mm., D_{15}^{15} 0·9536. *Propyl β-propoxypropionate* is a colourless, agreeably smelling liquid, b. p. 74·5—75·5°/7 mm., D_{15}^{15} 0·9386 N. C.

A Green, Crystalline Manganitartrate. ANDRÉ JOB and P. GOISSEDET (*Compt. rend.*, 1911, **152**, 265—268. Compare Abstr., 1907, ii, 553; Durrant, Trans., 1905, **87**, 1781).—Eighteen grams of manganous sulphate dissolved in water (20 c.c.) are added to a solution of sodium tartrate (450 grams) in a litre of water. The solution is shaken in an atmosphere of oxygen, and 100 grams of sodium hydroxide in 250 c.c. of water added slowly. The red liquid gradually deposits green crystals of *sodium manganitartrate*,

$$\begin{matrix} CO_2Na\cdot CH\cdot O \\ | \\ CO_2Na\cdot CH\cdot O \end{matrix}\!\!>Mn\cdot O\cdot CH(CO_2Na)\cdot CH(ONa)\cdot CO_2Na,11H_2O.$$

This salt dissolves in water, forming an alkaline solution, which deposits manganic hydroxide and probably, through hydrolysis having occurred, contains the salt, $\begin{matrix} CO_2Na\cdot CH\cdot O \\ | \\ CO_2Na\cdot CH\cdot O \end{matrix}\!\!>Mn\cdot OH$. On the addition of sodium tartrate the liquid becomes green and remains stable. The green solutions are unable to afford green crystals, although these appear on the addition of an alkali carbonate, when the liquid becomes red. An explanation of this fact is suggested.

W. O. W.

Basic Citrates and Tartrates of Barium. ANTONIO QUARTAROLI (*Chem. Zentr.*, 1910, ii, 1131—1132; from *Staz. sperim. agrar. ital.*, 1910, **43**, 396—408).—The author states than when excess of barium hydroxide is added to a solution of citric acid at a temperature of at least 18°, a tetrabasic citrate is formed; at lower temperatures (+5—10°) a less basic citrate is formed, which is more soluble. The citrate formed above 18° dissolves to the extent of 10—13% in water. With tartaric acid, in the same way, a tribasic tartrate is obtained; the same modification is formed at 18° and at 5—10°, but at 100° a crystalline form is obtained. N. C.

Preparation of Formaldehyde from Methyl Alcohol by the Contact Process. MAX LE BLANC and E. PLASCHKE (*Zeitsch. Elektrochem.*, 1911, **17**, 45—57).—A constant, measured current of air is passed through methyl alcohol, kept at a constant temperature. The mixture of air and alcohol vapour, then passes over a spiral of silver, silver-plated copper, or copper gauze, and the products (consisting of formaldehyde, unchanged methyl alcohol, carbon monoxide and dioxide, hydrogen and nitrogen) are collected and analysed.

The maximum yield of formaldehyde is always obtained at about the same temperature. Measured near the end of the silver gauze spiral at which the gases entered it, the best temperature is 450°, but this is not the maximum temperature of the spiral, which often reaches a bright red heat in the middle. When the temperature of the contact is kept constant and the ratio of air to alcohol in the mixture is gradually increased, the yield of aldehyde increases to a maximum and then diminishes again. The maximum yield is obtained with about 0·46 gram of oxygen to 1 gram of alcohol. The loss of alcohol (the part not accounted for by aldehyde or unchanged alcohol in the products) increases rapidly and continuously as the oxygen is increased. The length of the contact layer also affects the results; in the 30 mm. tube used by the authors, the most favourable length was 70 mm., which gave the highest yield of formaldehyde observed, namely, 58% of the theoretical quantity.

The results with copper were very similar to those obtained with silver, the best length of layer being 80—90 mm., and the best mixture containing 0·39 gram of oxygen per gram of methyl alcohol.

A consideration of the composition of the gaseous products (which always contain more hydrogen than the sum of the carbon monoxide and dioxide) leads to the conclusion that the formation of formaldehyde is due, not to oxidation of methyl alcohol, but rather to its decomposition, thus: $CH_3{\cdot}OH = CH_2O + H_2$. The main source of loss is the decomposition of formaldehyde by heat: $CH_2O = CO + H_2$. To test this, methyl alcohol vapour was passed over freshly reduced copper at 700°. The yield of formaldehyde is fairly good at first, but falls off rapidly. (In six experiments with the same spiral, it fell from 28% in the first to 4% in the sixth.) The activity of the copper is restored by oxidising it and reducing it again. It appears, therefore, that the function of the air in the usual contact process is to keep the copper constantly in its most active form by continually oxidising it, the reduction being brought about by the hydrogen and carbon monoxide present. T. E.

Electrosyntheses. VI. Sima M. Losanitsch (*Ber.*, 1911, **44**, 312—315. Compare Abstr., 1910, i, 542).—It has been shown previously (Abstr., 1897, i, 179) that under the action of the silent discharge a mixture of carbon monoxide and hydrogen gives formaldehyde, which immediately condenses to yellow aldehydic products. Further investigation shows that these products consist of a liquid portion, soluble in water, alcohol and ether, and a solid portion, which is only soluble in water. The liquid portion is viscous, has the odour of paraldehyde, and contains formic acid. The yellow, solid portion has a composition corresponding with $C_{12}H_{18}O_{11}$. It is probably the first anhydride of $C_6H_{12}O_6$, since cryoscopic experiments show that the freshly made aqueous solution contains molecules corresponding with $C_{12}H_{18}O_{11}$, and these, on keeping, split up into $C_6H_{12}O_6$ molecules. Evaporation of the aqueous solution on the water-bath leaves a dark residue with the composition $C_6H_8O_5$; if the evaporation is carried out in a vacuum, the yellow compound, $C_{12}H_{18}O_{11}$, is left.

The aqueous solution of the yellow solid readily gives glyoxal

phenylosazone with phenylhydrazine, and glyoxime with hydroxylamine, from which it is probable that the yellow solid is a readily decomposable condensation product of glyoxal.

The formaldehyde produced from the carbon monoxide and hydrogen by the silent discharge probably condenses to the two following aldehydes: $2CH_2O = OH{\cdot}CH_2{\cdot}CHO$ and $2CH_2O = CHO{\cdot}CHO + H_2$, and these then form the compound $CHO{\cdot}CHO,2OH{\cdot}CH_2{\cdot}CHO$, which is the yellow solid.

The condensation product obtained from carbon monoxide and methane (Abstr., 1908, i, 866) also contains a part soluble and a part insoluble in water. The former is identical with the above yellow solid, $C_{12}H_{18}O_{11}$.

A mixture of carbon dioxide and hydrogen behaves similarly to a mixture of carbon monoxide and hydrogen towards the silent discharge, since the carbon dioxide is first reduced to the monoxide.

T. S. P.

α-Bromocrotonaldehyde. PAUL L. VIGUIER (*Compt. rend.*, 1911, **152**, 269—271. Compare Abstr., 1909, i, 691; 1910, i, 461).—α-Bromocrotonaldehyde forms an *oxime*, m. p. 110—111°, which becomes pasty on keeping. The *semicarbazone* has m. p. 228—230°. 5-Methylpyrazole is produced when the aldehyde is added to an alcoholic solution of hydrazine hydrate. The *phenylhydrazone*, lamellæ, m. p. 124—125°, is unstable; when treated with alcoholic potassium hydroxide, it forms 1-phenyl-5-methylpyrazole; on heating with excess of phenylhydrazine, it furnishes a *compound*, $C_{16}H_{18}N_4$, m. p. 117—119°.

When α-bromocrotonaldehyde or its acetal is allowed to act on urethane in aqueous solution in presence of a little hydrochloric acid, a *compound*, $C_{13}H_{24}O_6N_3Br$, is obtained. This crystallises in colourless, slender needles, m. p. 124—125°, and is useful for characterising the aldehyde.

W. O. W.

Photochemical Synthesis of Carbohydrates from Carbon Dioxide and Hydrogen in the Absence of Chlorophyll. JULIUS STOKLASA and WENZEL ZDOBNICKÝ (*Biochem. Zeitsch.*, 1911, **30**, 433—456; *Monatsh.*, 1911, **32**, 53—75).—A figure is given of the apparatus employed for carrying out experiments in the presence of ultra-violet light, the chief feature of which is the form of the basin in which the reactions were investigated, which was suspended from a mercury-quartz lamp which served as the source of light. It was found that water does not act on carbon dioxide in ultra-violet light in the absence of potassium hydroxide, neither formaldehyde nor carbohydrate being formed in this case. If potassium hydroxide is added, however, formaldehyde, but no carbohydrate, is formed. The hydrogen must be in the nascent state for the reaction to take place, and ultra-violet light must be present. In the absence of the latter, formic acid is formed. A sugar is also formed when nascent hydrogen reacts with carbon dioxide in the presence of ultra-violet rays. The nature of the carbohydrate has not yet been definitely established. The osazone melts at 196—200°, and is not, therefore, either formose, β-formose, or β-acrose.

S. B. S.

Nomenclature of the Sugars. EMIL VOTOČEK (*Ber.*, 1911, **44**, 360—361).—The prefix *epi* is used to denote the new carbohydrate formed by the interchange of the H and OH groups on the α-carbon atom; thus mannose becomes *epi*glucose, ribose becomes *epi*arabinose, talose becomes *epi*galactose, etc. The isomeric pair are spoken of as *epimerides*, and the change as *epimerism*. The nomenclature is extended to the alcohols and acids of the carbohydrates. E. F. A.

***epi*Rhodeose.** EMIL VOTOČEK and CYRILL KRAUZ (*Ber.*, 1911, **44**, 362—365. See preceding abstract).—Rhodeonic acid, prepared by oxidation of rhodeose with bromine, is partly converted on heating with pyridine at 150—160° into epi*rhodeonic acid*. The *barium* salt forms colourless, matted crystals, which are optically inactive. The crystalline *lactone* is reduced by sodium amalgam in the usual manner to epi*rhodeose*; this is a syrup, yielding the same phenylosazone as rhodeose, but the *methylphenylhydrazone* has m. p. 175°. On oxidation with nitric acid, the trihydroxyglutaric acid obtained has m. p. 184—185°, $[\alpha]_D$ +12°, falling to +2·5° on boiling, and differs slightly from the inactive lactone described by Fischer and Piloty (m. p. 170—171°; compare Abstr., 1892, 440). It is pointed out that ribohydroxyglutaric acid, although itself completely symmetric, forms a lactone, which is not symmetric. Fischer's lactone is an equimolecular mixture of *d*- and *l*-lactones, but that from *epi*rhodeose is possibly completely derived from *d*-lactone or from a mixture of *d*- and *l*-lactones in unequal proportions. E. F. A.

Solubility of Lime in Aqueous Solutions of Sucrose and of Glycerol. FRANK K. CAMERON and HARRISON E. PATTEN (*J. Physical Chem.*, 1911, **15**, 67—72).—When lime in excess is added to sucrose solution, a soluble compound of lime and sugar is formed, but some of the sucrose passes into the solid phase. The relation between the amount of lime dissolved and the amount of sucrose in solution is not a linear one, since the liquid is in equilibrium with a series of solid solutions of the lime-sucrose compound in lime. The solid phase, consisting of fine globular granules, was separated by a centrifuge, and contained upwards of 10·8% of sucrose.

Solutions containing more than 20% of sucrose could not be investigated owing to their high viscosity. The 20% solution dissolves about 6% of lime at 25°.

The presence of glycerol increases the solubility of lime to 1·34% in a 55% solution of glycerol. The ratio of lime to glycerol is a strictly linear one, and no glycerol passes into the solid phase. R. J. C.

Cellobiose and the Acetolysis of Cellulose. WILHELM SCHLIEMANN (*Annalen*, 1911, **378**, 366—381).—The treatment of cellulose (filter-paper or cotton wool) with a mixture of acetic anhydride and concentrated sulphuric acid at low temperatures yields products quite different from those obtained at higher temperatures, because the acetolysis (that is, the acetylation and hydrolysis of the cellulose molecule) is less quickened by the sulphoacetic acid produced in the acetylating mixture at high temperatures (Stillich,

Abstr., 1905, i, 318; 1906, i, 552, 626) than by the acetylsulphuric acid formed at low temperatures.

The product obtained by acetylating cellulose by Skraup and König's method (Abstr., 1902, i, 135) or by Maquenne and Goodwin's process (Abstr., 1904, i, 799), after hydrolysis by alcoholic potassium hydroxide, yields cellobiose, which, after being completely dried at 100°, has the formula $C_{12}H_{22}O_{11}$, and $[\alpha]_D^{20}$ 34·6° in 2—17% aqueous solutions. It can be estimated by Fehling's solution by Wein's method, and forms a *phenylosazone*, m. p. 208—210°, $[\alpha]_D$ −17·5° in alcoholic solution.

By treatment with acetic anhydride and sulphuric acid (or a little zinc chloride) it yields the same octa-acetylcellobiose, m. p. 221·5—222°, $[\alpha]_D^{20}$ 41·5° in chloroform, as is produced by the action of this acetylating mixture on cellulose (Maquenne and Goodwin, *loc. cit.*). The isomeric octa-acetylcellobiose, m. p. 191·5—192°, obtained by boiling cellobiose with acetic anhydride and sodium acetate, has $[\alpha]_D^{20}$ −7·8° in chloroform and −24·9° in benzene. Both octa-acetylcellobioses can be converted into the acetochloro-compound, m. p. 186—187° (Geinsperger, Abstr., 1906, i, 57; Hardt-Stremayr, Abstr., 1907, i, 389), from which, according to the author, silver acetate produces the octa-acetylcellobiose, m. p. 191°, $[\alpha]_D^{20}$ −7·5° in chloroform, whilst Geinsperger obtained an acetate, $[\alpha]_D$ −30·05° in chloroform, and Hardt-Stremayr an acetate, $[\alpha]_D$ 30·51°; the discrepancy is inexplicable.

In view of Jungius' experiments on the equilibrium of the penta-acetyldextroses (Abstr., 1905, i, 573), cellobiose and its two octa-acetyl derivatives have been treated with acetic anhydride and sulphuric acid, acetic anhydride and zinc chloride, and acetic anhydride and sodium acetate. The last-mentioned reagent does not change either of the octa-acetylcellobioses once it has been formed; with the other two reagents, mixtures of the two acetates are obtained, containing respectively 84% and 77% of the octa-acetyl compound, which has $[\alpha]_D^{20}$ 41·5° in chloroform. The two acetates in the mixture can be separated by cold benzene, in which the acetate, m. p. 191°, $[\alpha]_D^{20}$ −7·7° in chloroform, is the more soluble. Evidence is stated which indicates that the octa-acetylcellobiose, m. p. 191°, belongs to the β-series.

The amorphous by-products, obtained in addition to octa-acetylcellobiose by the acetolysis of cellulose, have been examined in regard to the content of acetic acid liberated by hydrolysis; the author is of opinion that the products containing 66·3—67·3% of acetic acid are the immediate precursors of the octa-acetylcellobiose. C. S.

Action of Water and of Alkali on Cotton Wool Cellulose.

CARL G. SCHWALBE and MICHAEL ROBINOFF (*Zeitsch. angew. Chem.*, 1911, **24**, 256—258. Compare Tauss Dingler's *Polyt. Jour.*, 1889, **273**, 276; 1890, **276**, 411).—It is shown that the formation of hydrocelluloses, that is, compounds with strongly reducing properties, under the influence of water occurs only when the cellulose is partly altered; for example, filter-paper or strongly-bleached cellulose. With pure cellulose the formation of hydrocellulose is extremely small, even

under a pressure of 20 atmospheres. When a temperature of 150° is reached, marked decomposition of the cellulose occurs.

The action of dilute sodium hydroxide solutions on cellulose has been studied; the maximum effect at the ordinary temperature is obtained with a 4% alkali solution, as shown by the fact that the product after such treatment gives the highest copper values (corrected). At temperatures of 100° and above, the solubility increases, but diminishes as the concentration of the alkali is increased; at 150° the solubility is appreciable. The "gum value" has been obtained for a number of samples; by gum value is understood the weight of amorphous precipitate obtained by neutralising the alkaline extract. Pure cellulose has a "gum value" of practically nil, whereas impure forms have higher values. At 150°, however, the differences are small, and here it is also noticeable that the 4% alkali has the maximum effect. In treatment of cellulose, temperatures above 150°, and an alkali concentration of 4% are to be avoided. The acid used after bleaching should not be stronger than 0·1%; with still more dilute acid, a purer white is obtained, but the amount of oxycellulose is increased. J. J. S.

Action of Hydracids on Starch. II. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 848—849. Compare Abstr., 1910, i, 655).—Starch (1·7 grams), water (50 grams), and hydrochloric acid (2 c.c.) after being left for seven minutes at 18·5° and then heated for four minutes gave a reddish-orange precipitate with Fehling's solution. Hydrobromic acid (1·5 c.c.) behaved similarly; hydriodic acid (1 c.c.) produced only a slight, although distinct, precipitate. After four hours at 17°, each acid had acted on starch sufficiently to cause slight reduction of Fehling's solution. E. F. A.

Dextrin. WILLIAM OECHSNER DE CONINCK and A. REYNAUD (*Bull. Acad. roy. Belg.*, 1910, 846—847).—A mixture of 0·8 gram of dextrin, 40 grams of water, and twenty drops of concentrated hydrochloric acid gave a yellow precipitate with Fehling's solution (Cu_2O,H_2O) after twenty-four hours at 22°. With hydrobromic acid (twelve drops) the reduction (Cu_2O) was marked in five hours; with five drops of hydriodic acid, cuprous oxide (Cu_2O) was precipitated after five minutes' or five hours' action. With five drops of hydrochloric acid the precipitate with Fehling's solution was cuprous oxide; with ten drops, it consisted of a mixture of cuprous oxide and its hydrate, and with fifteen drops, it was entirely the hydrated oxide, Cu_2O,H_2O.

E. F. A.

Formation of Crystalline Polysaccharides (Dextrins) from Starch Paste by Microbes. FRANZ SCHARDINGER (*Centr. Bakt. Par.*, 1911, ii, 29, 188—197).—Certain micro-organisms convert starch paste into substances soluble in water closely resembling dextrins. *Bacillus macerans* renders potato-starch completely soluble, arrowroot-starch nearly completely so, but has far less effect on rice and wheat starch. Part of the dextrin formed, about 25—30% of the starch taken, is crystalline, the rest being amorphous and gum-like. Two different crystalline dextrins distinguished as α and β have been

obtained from all four varieties of starch, the α-isomeride predominating. It crystallises in colourless, hexagonal plates or lancet-shaped needles, and is doubly refractive, $[\alpha]_D + 128°$; the coloration of the crystalline precipitate with iodine is blue in thin layers when wet, greyish-green when dry. The β-isomeride crystallises in reniform aggregates of rhombic crystals, $[\alpha]_D + 136°$; the crystalline precipitate with iodine is a reddish-brown both wet and dry; it sinters and decomposes at 260°.

Both dextrins are precipitated from aqueous solution by alcohol, ether, chloroform, and iodine solution; they do not reduce Fehling's solution, and are not fermented by yeast. E. F. A.

Tellurium. ALEXANDER GUTBIER and FERDINAND FLURY (*J. pr. Chem.*, 1911, [ii], 83, 145—163. Compare Abstr., 1907, ii, 255).—The majority of the results recorded by previous investigators on the tellurichlorides and the telluribromides of the alkali metals and of aliphatic ammonium compounds have been confirmed; the existence of Rammelsberg's compounds, $8KCl,3TeCl_4$ and $8NH_4Cl,3TeCl_4$, and of the hydrated potassium tellurichloride described by von Hauer and by Wheeler (Abstr., 1893, ii, 457) is denied.

The salts described below are prepared by mixing an excess, generally one half to three-quarters, of a solution of carefully purified tellurium dioxide in the halogen acid with a solution of the alkali or substituted ammonium halide; with suitably selected concentrations, the desired salt crystallises more or less rapidly and is recrystallised from the dilute halogen acid. The tellurium is estimated by Lenher and Homberger's process (Abstr., 1908, ii, 426). The salts are characterised by their splendid colour and crystallise well, generally in the regular system. They dissolve without decomposition in a small quantity of water at the ordinary temperature or by gentle warming, but are extensively decomposed by even a small excess of water with the separation of tellurous acid. The telluribromides are stable in the air.

[With H. MICHELER.]—The following salts have been obtained: Ammonium tellurichloride is prepared best from dilute solutions and by spontaneous evaporation; it crystallises in sulphur-yellow octahedra. *Trimethylammonium tellurichloride*, $2NMe_3,H_2TeCl_6$, pale yellow needles; *diethylammonium*, $2NHEt_2,H_2TeCl_6$, sulphur-yellow, monoclinic crystals; *triethylammonium*, $2NEt_3,H_2TeCl_6$, yellow needles; *propylammonium*, $2NH_2Pr^{\alpha},H_2TeCl_6$, yellow, rhombic plates; iso*propylammonium*, $2NH_2Pr^{\beta},H_2TeCl_6$, greenish-yellow, monoclinic plates; *dipropylammonium*, $2NHPr^{\alpha}_2,H_2TeCl_6$, yellow, rhombic (or tetragonal) crystals; *butylammonium*, $2C_4H_9 \cdot NH_2,H_2TeCl_6$, long, pale yellow needles; iso*butylammonium*, $2C_4H_9 \cdot NH_2,H_2TeCl_6$, like the preceding salt. *Diethylammonium telluribromide*, $2NHEt_2,H_2TeBr_6$, orange-red needles; *triethylammonium*, $2NEt_3 \cdot H_2TeBr_6$, orange-red, monoclinic crystals; *propylammonium*, $2NH_2Pr^{\alpha},H_2TeBr_6$, orange-red plates; iso*propylammonium*, $2NH_2Pr^{\beta},H_2TeBr_6$, orange-red, tetragonal needles; *dipropylammonium*, $2NHPr_{\alpha 2},H_2TeBr_6$, orange-red, monoclinic plates; *butylammonium*, $2C_4H_9 \cdot NH_2,H_2TeBr_6$, orange-red needles; iso*butylammonium*, $2C_4H_9 \cdot NH_2,H_2TeBr_6$, orange-red plates. C. S.

Salts of Pertitanic Acid with Organic Bases. EDUARD KUROWSKI and L. NISSENMANN (*Ber.*, 1911, **44**, 224—229).—The authors describe the preparation and properties of a number of salts of pertitanic acid with primary and secondary aliphatic amines. The method of preparation adopted consists in the gradual addition of a mixture of the amine and 30% hydrogen peroxide to titanium trioxide and subsequent precipitation of the salt by the addition of a mixture of alcohol and ether, the temperature being maintained at $-10°$ to $-15°$.

The salts are all unstable, dissolve in water with a green colour, and decompose rapidly at the ordinary temperature. They dissolve in dilute sulphuric acid with the formation of hydrogen peroxide.

The *methylamine* salt, $(NH_3Me\cdot O)_2TiO_4,3H_2O$, has a yellowish-green colour; when exposed to the air it forms oily drops, and then decomposes with the liberation of carbon.

The *ethylamine* salt, $NH_3Et\cdot O\cdot TiO_4H,1\frac{1}{2}H_2O$, is a yellow powder.

The *propylamine* salt, $2NH_3Pr^{\alpha}\cdot O\cdot TiO_4H,H_2O_2,2H_2O$, has a yellowish-green colour; a second less stable salt has also been obtained.

Of the salts with secondary aliphatic amines, only the *diethylamine* salt, $2NH_2Et_2\cdot O\cdot TiO_4H,H_2O_2,14H_2O$, was obtained in a pure condition; it is a yellow powder.

The *dimethylamine* and *dipropylamine* salts so readily decompose that their composition has not been determined.

Attempts to prepare salts of pertitanic acid with tertiary amines and also with aniline were unsuccessful. F. B.

Ruthenihalides. ALEXANDER GUTBIER [with G. A. LEUCHS] (*Ber.*, 1911, **44**, 306—308).—The following compounds were prepared according to a method previously described (Abstr., 1907, i, 289):

Triethylammonium ruthenichloride, $(NHEt_3)_2RuCl_6$, forms large, broad, blackish-red plates. *Triethylammonium ruthenibromide*,

$(NHEt_3)_2RuBr_6$,

crystallises in large, black plates. iso*Propylammonium ruthenichloride*, $(NH_3Pr^{\beta})_2RuCl_6$, forms glistening, dark greenish-brown or black needles. iso*Propylammonium ruthenibromide*, $(NH_3Pr^{\beta})_2RuBr_6$, is obtained in dark bluish-black needles. n-*Butylammonium ruthenichloride*, $(C_4H_9\cdot NH_3)_2RuCl_6$, forms dark, greenish-brown, glistening needles. n-*Butylammonium ruthenibromide*, $(C_4H_9\cdot NH_3)_2RuBr_6$, forms deep bluish-black needles. *Benzylammonium ruthenichloride*,

$(C_7H_7\cdot NH_3)_2RuCl_6$,

crystallises in greenish-brown, slender needles. *Benzylammonium ruthenibromide*, $(C_7H_7\cdot NH_3)_2RuBr_6$, forms black, felted needles. *Pyridinium ruthenichloride*, $(C_5H_6N)_2RuCl_6$, forms brown needles *Pyridinium ruthenibromide*, $(C_5H_6N)_2RuBr_6$, crystallises in light bluish-black needles. *a-Picolinium ruthenichloride*,

$(C_5NH_5Me)_2RuCl_6$,

is obtained in small, bronze-coloured leaflets. *a-Picolinium ruthenibromide*, $(C_5NH_5Me)_2RuBr_6$, forms shining, bluish-black needles.

T. S. P.

Labile Hydrated Forms Fixed by means of an Organic Base. GIUSEPPE A. BARBIERI and F. CALZOLARI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 584—590).—The authors have acted on various metallic salts in aqueous solution with hexamethylenetetramine, and on the hypothesis that this substance combines with hydrates already existing in the solution, the composition of the solid substances which separate yields information as to the nature of the hydrates in question (compare Kurnakoff, Abstr., 1898, ii, 475). The following facts accord with the supposition that the hexamethylenetetramine is not united with the metallic atom, but is added to the molecule of the hydrated salt present in the solution: (1) anhydrous cobalt chloride forms with hexamethylenetetramine a compound in which the base is attached to the metal, and this compound is blue; (2) a compound, $(AcONa,3H_2O)_2C_6H_{12}N_4$, exists, and it is not probable that the base could be attached to sodium; (3) with salts which usually are anhydrous, or give hydrates containing little water, hexamethylenetetramine compounds are obtained which contain little or no water. The compounds described are, therefore, to be regarded as amines of hydrated salts.

The following compounds are prepared by acting on concentrated (20%) aqueous solutions of the chlorides, bromides, and iodides of magnesium, manganese, cobalt, and nickel with concentrated aqueous solutions of hexamethylenetetramine (2—4 mols.). They form large, measurable crystals, which are not deliquescent. The tendency to effloresce in contact with dehydrating agents is greatest in the case of the chlorides, least with the iodides, which are stable to air and light. In solution, the manganese derivatives gradually deposit manganous hydroxide. The *compound*, $MgCl_2,10H_2O,2C_6H_{12}N_4$, forms colourless, transparent, tabular crystals belonging to the triclinic system (holosymmetric):

$$[a:b:c = 0{\cdot}8321:1:0{\cdot}8573;\ \alpha = 125°43',\ \beta = 50°21',\ \gamma = 123°56'].$$

The *compound*, $MnCl_2,10H_2O,2C_6H_{12}N_4$, forms minute crystals of a pale flesh colour. The *compound*, $CoCl_2,10H_2O,2C_6H_{12}N_4$, crystallises in reddish-violet laminæ, which in contact with phosphoric oxide lose all their water and become intensely blue. The *compound*,

$$NiCl_2,10H_2O,2C_6H_{12}N_4,$$

crystallises in green laminæ, which on dehydration in an oven become first yellow, then violet. The *compound*,

$$MgBr_2,10H_2O,2C_6H_{12}N_4,$$

forms plates which are almost square; they belong to the monoclinic system (holosymmetric): $[a:b:c = 0{\cdot}9022:1:0{\cdot}5111;\ \beta = 90°40']$. The *compound*, $MnBr_2,10H_2O,2C_6H_{12}N_4$, forms almost colourless crystals. The *compound*, $CoBr_2,10H_2O,2C_6H_{12}N_4$, forms reddish-violet crystals. The *compound*, $NiBr_2,10H_2O,2C_6H_{12}N_4$, crystallises in green laminæ. The *compound*, $MgI_2,10H_2O,2C_6H_{12}N_4$, forms long, colourless, transparent crystals, which belong to the monoclinic system (holosymmetric): $[a:b:c = 0{\cdot}8802:1:0{\cdot}495;\ \beta = 90°1']$. The *compound*,

$$MnI_2,10H_2O,2C_6H_{12}N_4,$$

is a white powder. The *compound*, $CoI_2,10H_2O,2C_6H_{12}N_4$, forms rose-coloured, tabular crystals. The *compound*,

$$NiI_2,10H_2O,2C_6H_{12}N_4,$$

forms emerald-green crystals. In some cases where the analytical results do not permit of the exact determination of the amount of contained water, the question can be settled from relations of isomorphism and power to form mixed crystals which exist between many of the substances. The crystallographic measurements were executed by E. Billows. R. V. S.

Alkylation of Acid Amides. MOTOOKI MATSUI (*Mem. Coll. Sci. Eng. Kyoto*, 1910, **2**, 397—400).—In the alkylation of amides, silver oxide may be replaced by cuprous oxide, lead oxide, or anhydrous potassium carbonate.

When a mixture of acetamide and ethyl iodide is heated for three to four hours on the water-bath with one of these substances, ethyl imino-acetate is produced. Benzamide, under the same conditions, yields ethyl iminobenzoate.

It is therefore highly probable that in alkylating with silver oxide and an alkyl iodide, the silver oxide accelerates the reaction merely by the removal of the hydriodic acid produced, and not by the intermediate formation of a silver derivative (compare Lander, Trans., 1900, **77**, 729).

The author considers it probable that the formation of imino-esters by the action of methyl sulphate on amides is due to the direct alkylation of the enolic form: $NH{:}CR{\cdot}OH$, and not to the addition of methyl sulphate to the ketonic form, as suggested by Bühner (Abstr., 1904, i, 882). F. B.

Formation and Decomposition of Calcium Cyanamide. MAX LE BLANC and M. ESCHMANN (*Zeitsch. Elektrochem.*, 1911, **17**, 20—34).—It is shown that the reaction $CaC_2 + N_2 \rightleftarrows CaCN_2 + C$ is reversible. The equilibrium pressure of nitrogen, however, is dependent on the quantity of nitrogen which has been taken up by the carbide. Measurements of the pressures are made at 1200° and 1300°. After almost saturating a quantity of carbide with nitrogen, successive quantities of nitrogen are removed from it by diminishing the pressure, and the corresponding equilibrium pressures are measured; the quantity of combined nitrogen is then increased by adding fresh nitrogen, and the pressures again measured. The two curves do not agree with each other, the pressure corresponding with a given percentage of combined nitrogen constantly decreases with the duration of the experiments; apparently the cyanamide becomes more stable. A careful chemical examination of the reaction shows that the reversible formation of calcium cyanamide is really the reaction being observed, but the calcium cyanamide gradually volatilises out of the mixture and condenses in the cooler parts of the apparatus, where it can no longer decompose, partly owing to the lower temperature and partly owing to the absence of carbon. T. E.

Some Solid Ammoniates. CARLO GASTALDI (*Gazzetta*, 1910, **40**, ii, 475—481).—When a concentrated aqueous solution of potassium ferricyanide is added to an ammoniacal solution of silver nitrate, a fine-grained, deep red, crystalline precipitate is deposited, which has the

composition $2[Ag_3Fe(CN)_6],5NH_3$. By varying the conditions, the substance can be obtained as an amorphous, flocculent precipitate, or, by dissolving freshly precipitated silver ferricyanide in ammonia and evaporating the solution at the ordinary temperature, in large crystals. In all cases the composition is the same. When the ammonia is replaced by methylamine or ethylamine, *methyl-* and *ethyl-ammoniates* of similar composition are obtained.

The qualitative test for the ferricyanic radicle may be masked by the presence of simple cyanides in a solution under investigation. If aluminium and hydrochloric acid are added to the liquid, however, the production of a coloration with an iron salt will indicate the presence of a ferricyanide, for in these circumstances the formation of the complex from a cyanide and the iron salt cannot occur. R. V. S.

Action of Hydroxylamine on Nitrosochlorides and Nitrosates. III. αβ-Amylenehydroxylamineoxime and Derivatives. Guido Cusmano (*Gazzetta*, 1910, **40**, i, 525—536. Compare Abstr., 1910, i, 863).—*β-Hydroxylamino-β-methylbutan-γ-oneoxime* (*amylenehydroxylamineoxime*), $OH\cdot NH\cdot CMe_2\cdot CMe\colon N\cdot OH$, is prepared by suspending amylene nitrosate in a mixture of methyl alcohol and ether containing hydroxylamine (2 mols.). The reaction commences on warming, and then proceeds spontaneously. After removal of the solvent, the residue is dissolved in a little water and treated with sodium carbonate to dissolve the hydroxylamine nitrate present, and from the solution β-hydroxylamino-β-methylbutan-γ-oneoxime crystallises out on cooling. It forms rhombohedra, or laminar, hexagonal prisms, m. p. about 112° (previously softening), and reduces Fehling's solution readily in the cold. The *hydrochloride*, $C_5H_{12}O_2N_2,HCl$, forms clusters of crystalline leaflets, m. p. 125—130°, and are very deliquescent. The *nitroso-oxime* is obtained as an oil of a blue tinge by oxidising the hydroxylamino-oxime with the calculated quantity of permanganate. The p-*nitrobenzylidene* derivative, $OH\cdot N\colon C_5H_9\cdot \underset{\diagdown O \diagup}{N{-}C}\cdot C_6H_4\cdot NO_2$ (from *p*-nitrobenzaldehyde), forms pale yellow, hexagonal laminæ, m. p. about 187°. It dissolves in alkalis, producing a red coloration.

β-Hydroxylamino-β-methylbutan-γ-oneoxime reacts readily with nitrous acid, yielding *β-nitrosohydroxylamino-β-methylbutan-γ-oneoxime*, $OH\cdot N(NO)\cdot CMe_2\cdot CMe\colon N\cdot OH$, which is a very stable substance, crystallising in long, colourless needles, m. p. 81—82°. It does not reduce Fehling's solution, but yields a bluish-green coloration with a solution of phenol in sulphuric acid. It can be boiled with water without suffering decomposition, but it is readily decomposed by dilute acids even in the cold. It dissolves in sodium carbonate with effervescence, and the solution on concentration yields the *sodium* salt of the *iso*nitroamine. The *iso*nitroamine can displace nitrous acid, so that this sodium salt can be prepared by mixing concentrated solutions of hydroxylamino-oxime and sodium nitrite in the presence of a little sulphuric acid. It crystallises with $3H_2O$, which it loses at 116°. The *anhydrous* salt, $C_5H_{10}O_3N_3Na$, has m. p. 130° (decomp.).

β-Hydroxylamino-β-methylbutan-γ-oneoxime, when kept in an alcoholic ethereal solution saturated with hydrogen chloride, eventually deposits

a *hydrochloride*, $C_5H_{11}O_2N,HCl$, in tufts of long, acicular crystals, m. p. 145° (decomp.), which are not deliquescent. On treatment with sodium carbonate, a base is obtained, crystallising in long, colourless prisms, m. p. 96—98°. This base readily reduces Fehling's solution in the cold. To it is ascribed the constitution of *β-hydroxylamino-β-methylbutan-γ-one*, $OH\cdot NH\cdot CMe_2\cdot COMe$, and this is confirmed by the existence of a *p*-nitrobenzylidene derivative, $C_{12}H_{14}O_4N_2$, which crystallises in yellow, rectangular tablets, decomposing at 176°.

If hydroxylaminomethylbutanoneoxime is dissolved in concentrated alkali, and the solution after some days is treated with carbon dioxide, a precipitate is obtained, from which two substances can be isolated. One crystallises in small, colourless prisms, m. p. 96—100°, and from its composition and properties is *β-hydroxy-β-methylbutan-γ-oneoxime*, $OH\cdot CMe_2\cdot CMe\colon NOH$. The other *compound* forms long, colourless prisms, m. p. 184° (decomp.).

To explain the differences between the hydroxylamino-oximes of pinene and amylene and that of limonene, it is suggested that the two first, being saturated compounds, exist solely, or chiefly, as *trans*-forms, whilst the unsaturated limonene compound can also assume the labile *cis*-form. R. V. S.

Unsaturated Lead Alkyls. JULIUS TAFEL (*Ber.*, 1911, **44**, 323—337).—In his electrolytic experiments on organic substances with mercury or lead cathodes, the author has frequently observed the formation of small quantities of oily products; with lead cathodes the oil is red. At his suggestion, Renger (following abstract) has studied the formation of these oily products, and has obtained the red oil in larger quantities from acetone; he considers that it consists essentially of lead tetra-*iso*propyl, since lead di-*iso*propyl dibromide is produced from it by the action of bromine. Since the lead tetra-alkyl compounds are colourless and the formation of a di-alkyl compound from a tetra-alkyl has hitherto been unknown, the author has extended the investigation of these oils.

The apparatus consists of a glass cathodic vessel shaped like a separating funnel and provided with a closely fitting lead cover, through apertures in which are fitted a thermometer, an inlet-tube for the delivery of carbon dioxide into the cathodic compartment, and the porcelain anodic cell. The cathode consists of six strips of lead, and the anode of a lead cylinder. The anodic liquor is 20% sulphuric acid; the cathodic solution is a mixture of 20% sulphuric acid and acetone (in the case of higher ketones a little alcohol must also be added). The temperature is kept at 45—50°, and the cathodic current density at about 0·5 amp./sq. cm. During the experiment the cathodic solution is well agitated by a current of carbon dioxide, and the red oil collects together with a white precipitate at the bottom of the vessel. It is run out into an apparatus (figured and described), in which it can be washed with dilute potassium hydroxide and with water, dried over sodium sulphate, and filtered, all of the operations being performed with the exclusion of air. The purified product is a viscous oil with the colour of bromine and an unpleasant odour. It loses its red colour rapidly in the light, leaving a golden-yellow oil consisting

chiefly of lead tetra*iso*propyl. When rapidly heated, the red oil decomposes at 150° with separation of finely divided lead; it decomposes at 85° in a vacuum. In contact with oxygen, the oil becomes coated with a yellowish-brown, strongly alkaline skin. When a solution of the red oil in an indifferent solvent is treated with oxygen, it acquires a pale yellow colour, and after filtration contains lead tetra-*iso*propyl and lead di-*iso*propyl oxide; the latter is extracted with dilute acetic acid, and is isolated in the form of *lead di-*iso*propyl dibromide*, $PbPr^{\beta}Br_2$. This salt, which crystallises in felted needles and decomposes when kept, even in darkness, is also obtained by carefully treating the red oil in well-cooled ether or ethyl acetate with bromine until the latter only slowly disappears. The corresponding *dichloride*, *dinitrate*, and *chromate* are described. When the oxidised filtered solution of the red oil is distilled at 40° in a vacuum, and the yellowish residue, which exhibits the properties of lead tetra-*iso*propyl, is triturated with concentrated hydrochloric acid, *lead tri-*iso*propyl chloride*, $PbPr^{\beta}Cl$, is obtained. It has a very unpleasant odour, is more volatile with steam, and is less stable than the dichloride. The corresponding *iodide* is described. The author is of opinion that the red oil consists essentially of lead tetra-*iso*propyl together with about 20% of lead di-*iso*propyl, to which the colour is due.

Pure lead tetra-*iso*propyl has not been obtained on account of its great instability, but the behaviour of lead tetra-ethyl is quite analogous to that of the red oil mentioned above; thus with bromine (1 mol.) in well-cooled ether or ethyl acetate it yields *lead triethyl bromide*, $PbEt_3Br$, which crystallises in large, colourless needles, and has an unpleasant odour; with 2 mols. of the halogen, lead tetra-ethyl yields *lead diethyl dibromide*, $PbEt_2Br_2$, the properties of which are quite analogous to those of the di-*iso*propyl dibromide.

C. S.

Lead Alkyl Compounds from Methyl Ethyl Ketone and Diethyl Ketone. Georg Renger (*Ber.*, 1911, **44**, 337—338. Compare preceding abstract).—The electrolytic reduction of methyl ethyl ketone and of diethyl ketone (in the presence of alcohol) at lead cathodes proceeds in a manner quite analogous to that of acetone. The resulting red oils have been characterised by chlorination and bromination in chloroform or ether, whereby the following salts, which are even more unstable than the *iso*propyl compounds, have been obtained. *Lead tri-*sec.*-butyl chloride*, $Pb(C_4H_9)_3Cl$, forms pale yellow needles, has an unpleasant odour, and melts and suddenly explodes at about 130° when heated rapidly. *Lead di-*sec.*-butyl bromide*,

$$Pb(C_4H_9)_2Br_2,$$

crystallises in yellow needles. *Lead di-γ-amyl dibromide*, $Pb(C_5H_{11})_2Br_2$, obtained from the oil from diethyl ketone, forms extremely unstable, brownish-yellow crystals.

C. S.

Constitution of Copper Acetylide. II. Johannes Scheiber and Hans Reckleben [and, in part, K. Strauss] (*Ber.*, 1911, **44**, 210—223. Compare Scheiber, Abstr., 1908, i, 933).—Further experi-

ments have confirmed the existence of copper acetylide in the hydrated form C_2Cu_2,H_2O, and in the anhydrous form C_2Cu_2.

The fact that when the acetylide is decomposed by mild chemical reagents, for example, hydrogen sulphide and potassium cyanide, quantitative yields of acetylene are obtained, points to the conclusion that its constitution must be closely related to that of acetylene. No indication of the conversion of the hydrate into an aldehyde derivative has been observed, either by leaving in contact with water or ammonia, by drying, or under the influence of substances which may be present during its formation.

The structural formulæ of the compounds depend on that of acetylene. According to Nef's scheme, the anhydrous compound would be $Cu_2C\colon C\colon$, and the hydrate, $Cu_2C\colon C\cdots OH_2$.

The black carbonaceous material usually obtained when copper acetylide is decomposed is shown to be due to oxidation; if oxygen or oxidising substances are excluded during the preparation and decomposition of the acetylide, no carbonaceous residue is obtained. If, on the other hand, the water used contains dissolved air, or if the pure carbide is heated in an atmosphere of carbon dioxide at 100°, or if oxidising agents, such as cupric or ferric salts, are used for washing the acetylide, appreciable amounts of black residue are obtained (compare Söderbaum, Abstr., 1897, i, 309). Analyses of the carbonaceous compound agree with the formulæ $(C_{11}H_6O_3)_x$ for the product when dilute hydrochloric acid is used, and $(C_{11}H_5O_3)_2$ for the product when concentrated acid is used.

The detection by means of acetylene of copper in solutions of ammoniacal cupric salts reduced by means of hydroxylamine can be carried out at a dilution of 1 in 1,100,000, or in the presence of large quantities of ammonium acetate or tartrate, of 1 in 200,000.

J. J. S.

Sulphonation of Benzene. Robert Behrend and Martin Mertelsmann (*Annalen*, 1911, **378**, 352—365).—The sulphonation of benzene by pure, concentrated sulphuric acid at 240—250° results almost exclusively in the formation of the *m*-disulphonic acid, less than 1% of the para-isomeride being produced after one and a-half-hours' heating. The addition of a little mercury causes the formation of the *m*- and the *p*-disulphonic acids in the proportion 2 : 1; ferrous sulphate acts similarly, about 10% of benzene *p*-disulphonic acid being produced. The two acids are readily separated in the form of their sodium salts, since sodium benzene-*p*-disulphonate is practically insoluble in a concentrated solution of sodium benzene-*m*-disulphonate.

The two acids are interconvertible by heating with concentrated sulphuric acid and a little mercury at 240—250°, an equilibrium mixture of about 2 parts of the *m*-disulphonic acid and 1 part of the para-isomeride being formed; the same result is attained, but extremely slowly, in the absence of the mercury.

The sodium salts of both acids, by treatment with pure concentrated sulphuric acid at 240—250°, are converted into benzene-1 : 3 : 5-trisulphonic acid, which is also formed to some extent by heating benzene

with concentrated sulphuric acid and potassium pyrosulphate at 240—250°. C. S.

Action of Strong Tertiary Bases on Sulphonyl Chlorides. EDGAR WEDEKIND and D. SCHENK (*Ber.*, 1911, **44**, 198—202).—Triethylamine reacts with sulphonyl chlorides when dissolved in indifferent solvents, for example, benzene, provided a hydrogen atom is attached to the *a*-carbon atom with respect to the sulphonyl group. Hydrogen chloride is eliminated as in the case of the chlorides of carboxylic acids (Abstr., 1906, i, 437; 1909, i, 459), but the phenylsulphens, for example, $CHPh\colon SO_2$, cannot be isolated. With benzylsulphonyl chloride, stilbene is obtained by the elimination of sulphur dioxide and the union of the two CHPh: groups.

The chlorides of aromatic sulphonic acids do not react with tertiary bases.

Diphenylmethanesulphonic acid, $CHPh_2\cdot SO_3H,1\cdot 5H_2O$, crystallises from benzene in hygroscopic needles, m. p. 94—96°; when fused with potassium hydroxide, it yields *p*-hydroxydiphenylmethane (Trans., 1882, **41**, 34), and when heated with water at 240° for eight hours, it yields diphenylmethane. The acid chloride has not been prepared. Sodium sulphite solution and ω-chlorodiphenylmethane at 120—125° yield *benzhydrol ether*, $C_{26}H_{22}O$, m. p. 109°. J. J. S.

Phenanthrene-2-sulphonic Acid and Some of its Derivatives. HÅKAN SANDQVIST (*Annalen*, 1911, **379**, 79—90).—The phenanthrene-2-sulphonic acid used in the experiments is obtained in the form of the potassium salt from the by-products of the sulphonation of phenanthrene by Kunz's process. The acid is prepared from the acid chloride and water at 130—135°, from the barium salt and sulphuric acid, or from the lead salt and hydrogen sulphide. The acid contains H_2O, has m. p. about 150°, and is freed from its solvents only with difficulty; its electrical conductivity does not differ much from that of the 3-sulphonic acid (Abstr., 1909, i, 779). The following salts are described, the solubilities being expressed as before (*loc. cit.*): potassium ($\frac{1}{2}H_2O$), sol. 0·273; ammonium, sol. 0·37; *sodium* ($\frac{1}{2}H_2O$), white leaflets or needles, sol. 0·42; *calcium*, sol. 0·024; barium ($\frac{1}{2}H_2O$), sol. 0·016; *magnesium* ($6H_2O$), elongated leaflets, sol. 0·051; *zinc* ($6H_2O$), sol. 0·083; ferrous ($5H_2O$), sol. 0·044; lead (H_2O), sol. 0·014; *copper* (H_2O), bluish-green crystals, sol. 0·25; *silver*, sol. 0·099. *Phenanthrene-2-sulphonyl chloride*, obtained from the potassium salt and phosphorus pentachloride, has m. p. 156°, is oxidised by acetic and chromic acids to *phenanthraquinone-2-sulphonyl chloride*, yellow leaflets or needles, m. p. 245—246° (decomp.), and forms a *sulphonamide*, m. p. 253—254°, and *sulphonanilide*, $C_{14}H_9\cdot SO_2\cdot NHPh$, m. p. 157—158°, by the usual methods.

Methyl phenanthrene-2-sulphonate is dimorphous, the stable modification forming rhombic plates, the labile modification leaflets. The fact that many derivatives of phenanthrene have two m. p.'s may be due to dimorphism; the preceding ester, crystallised from methyl alcohol, has m. p. 92·5—93° and 101·5°, whilst in a capillary tube the m. p. is either 85°, 98°, or 101·5°. By oxidation with chromic

and acetic acids the ester yields *methyl phenanthraquinone-2-sulphonate*, yellow leaflets, m. p. 196—197°, or elongated leaflets, m. p. 192—192·5°. *Ethyl phenanthrene-2-sulphonate* has m. p. 88·5°.

C. S.

An Organo-metallic Compound of the Aniline Series. E. RATTENBURY HODGES (*Chem. News*, 1910, **103**, 52).—By slow addition of zinc chloride solution to a saturated aqueous solution of aniline, slender, colourless, highly refractive crystals of a compound of zinc chloride with aniline chloride were obtained. N. C.

Osmichlorides. ALEXANDER GUTBIER [with P. WALBINGER] (*Ber.*, 1911, **44**, 308—312).—The following osmichlorides were prepared by interaction of sodium osmichloride (Abstr., 1910, ii, 45) and aryl substituted ammonium chlorides. They were purified by recrystallisation from dilute hydrochloric acid; the aqueous sulutions undergo decomposition. The salts are all anhydrous and stable in the air.

Phenylammonium osmichloride, $(NH_3Ph)_2OsCl_6$, forms brownish-red, rhombic leaflets. *Phenylmethylammonium osmichloride*,

$(NH_3MePh)_2OsCl_6$,

forms brownish-red, monoclinic crystals, showing pleochroism. o-*Tolylammonium osmichloride*, $(C_6H_4Me\cdot NH_3)_2OsCl_6$, is obtained in yellow or brownish-red, rhombic needles, which are pleochroic. m-*Tolylammonium osmichloride* forms slender, pleochroic, brownish-red, rhombic needles. p-*Tolylammonium osmichloride* crystallises in yellowish-red, rhombic, pleochroic leaflets. o-4-*Xylylammonium osmichloride*,

$(C_6H_3Me_2NH_3)_2OsCl_6$,

forms shining red, monoclinic needles. m-4-*Xylylammonium osmichloride* forms strong, pleochroic, ruby-red, rhombic crystals. p-5-*Xylylammonium osmichloride* is obtained in red, rhombic, pleochroic needles. *Pyridinium osmichloride*, $(C_5H_6N)_2OsCl_6$, forms red, rhombic plates. *a-Picolinium osmichloride*, $(C_5NH_5Me)_2OsCl_6$, forms yellowish-red, rhombic leaflets. *Quinolinium osmichloride*, $(C_9NH_8)_2OsCl_6$, is obtained in yellowish-red, feebly pleochroic, monoclinic needles. *Benzylammonium osmichloride*, $(C_7H_7\cdot NH_3)_2OsCl_6$, forms brownish-red, monoclinic plates. *a-Naphthylammonium osmichloride*, $(C_{10}H_7\cdot NH_3)_2OsCl_6$, crystallises in brownish-red, pleochroic, rhombic needles. *β-Naphthylammonium osmichloride* forms brownish-red, pleochroic, rhombic leaflets. T. S. P.

Lactyl Compounds of Primary Aromatic Amines. KARL ELBS (*J. pr. Chem.*, 1911, [ii], **83**, 1—21) [with K. SINNER.]—The lactylation of several primary aromatic amines has been studied quantitatively at about 100° by heating mixtures of the amine and lactic acid, with or without water, in a water-bath and titrating the unchanged acid after definite intervals of time, phenolphthalein being used as indicator. In the experiments without water, the lactate of the amine is used. The results, which are expressed graphically, show that the formation of the lactyl compound is retarded by the presence of water, but is facilitated, contrary to Menschutkin's experience in the case of acetanilide, by using an excess of the amine (*p*-toluidine).

The lactylation of different amines under the same conditions, namely, 1 mol. of base, 1 mol. of acid, and 1·66 mols. of water at 100°, shows that the reactivity of the amino-group in aniline is affected slightly by the presence of a methyl group in the para-position, considerably and unfavourably by methyl in the ortho-position, and favourably by the ethoxy-group in the para- and still more so in the ortho-position.

[With Fr. Mette.]—Lactophenin in glacial acetic acid at 0° is converted by nitric acid, D 1·40, into 2-*nitro*-4-*ethoxylactanilide* (2-*nitrolactophenin*), $OEt{\cdot}C_6H_3(NO_2){\cdot}NH{\cdot}CO{\cdot}CHMe{\cdot}OH$, yellow needles or leaflets, m. p. 112°, the position of the nitro-group being determined by the fact that the substance and nitrophenacetin give the same nitrophenetidine by hydrolysis. Nitric acid, D 1·40, converts powdered lactophenin into 2 : 6-*dinitroethoxylactanilide*, yellow needles or leaflets, m. p. 135°, which yields the known dinitrophenacetin by hydrolysis and treatment of the product with acetic anhydride. Concentrated sulphuric and nitric acids at 0° convert dinitrolactophenin into the *nitrate*, $OEt{\cdot}C_6H_2(NO_2)_2{\cdot}NH{\cdot}CO{\cdot}CHMe{\cdot}ONO_2$, yellow leaflets, m. p. 192° (decomp.), which yields dinitrophenetidine, amongst other products, by hydrolysis with dilute alcoholic potassium hydroxide.

[With A. Schuster.]—3-*Nitrolacto*-p-*toluidide*,

$$NO_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}CO{\cdot}CHMe{\cdot}OH,$$

yellow needles, m. p. 86—87°, obtained from an acetic acid solution of lacto-*p*-toluidide and nitric acid, D 1·48, at 0°, yields 3-nitro-*p*-toluidine by hydrolysis. 3 : 5-*Dinitrolacto*-p-*toluidide*, yellow needles, m. p. 139—140°, obtained from the preceding compound and concentrated nitric and sulphuric acids at 0°, yields 3 : 5-dinitro-*p*-toluidine by hydrolysis. The *nitrate*, $C_6H_2Me(NO_2)_2{\cdot}NH{\cdot}CO{\cdot}CHMe{\cdot}ONO_2$, white needles, decomp. 160°, obtained from lacto-*p*-toluidide and concentrated sulphuric acid and nitric acid, D 1·48, at 0°, also yields 3 : 5-dinitro-*p*-toluidine by hydrolysis.

Owing to the ease with which lactotoluidides are hydrolysed even by dilute alkali, the electrolytic reduction of 3-nitrolacto-*p*-toluidide must be effected in an approximately neutral solution which is slightly alkaline in the immediate neighbourhood of the cathode. Even then the reduction does not proceed smoothly, for with an anodic liquid consisting of cold saturated sodium carbonate and a cathodic solution of acetic acid and sodium acetate, and a cathodic current density of 3—3·5 amperes per sq. dcm., the nitrolactotoluidide yields a number of products, from which 3 : 3′-*azoxylacto*-p-*toluidide*,

$$ON_2(C_6H_3Me{\cdot}NH{\cdot}CO{\cdot}CHMe{\cdot}OH)_2,$$

yellow needles or leaflets, m. p. 234° (decomp.), is isolated. By hydrolysis by dilute alcoholic potassium hydroxide, it yields 3 : 3′-*azoxy*-p-*toluidine*, red needles, m. p. 188°, which is converted by electrolytic reduction in sulphuric acid into the sparingly soluble sulphate of 3 : 4-tolylenediamine. The electrolytic reduction of 3-nitrolacto-*p*-toluidide in acid solution by Boehringer's process yields, amongst other products, acetaldehyde and 40—60% of 5-*methylbenziminazolone*,

$$C_6H_3Me{<}{}^{NH}_{NH}{>}CO,$$

white crystals, m. p. 292—295° (*acetyl* derivative, m. p. 176°), the

constitution of which is proved by the formation of the same substance from 3 : 4-tolylenediamine and carbamide.

[With Fr. Mette and A. Schuster.]—The electrolytic reduction of 2-nitroethoxylactanilide in approximately neutral (cathodic) solution at the b. p. yields 2 : 2′-*azoethoxylactanilide*,

$$N_2[C_6H_3(OEt)\cdot NH\cdot CO\cdot CHMe\cdot OH]_2,$$

yellowish-red needles, m. p. 269°, in 15—20% yield. By hydrolysis the azo-compound yields *azo*-p-*phenetidine*, m. p. 143°, which forms an acetyl derivative, m. p. 306°, identical with the azophenacetin obtained by the electrolytic reduction of nitrophenacetin.

The electrolytic reduction of 2-nitroethoxylactanilide in acid solution yields acetaldehyde, several unidentified products, one of which has m. p. 161°, and ethoxybenziminazolone (Cohn, Abstr., 1899, i, 944), the *diacetyl* derivative of which has m. p. 163°. C. S.

The Solubility of Sodium Picrate in Solutions of Sodium Salts. Woldemar Fischer and P. Miloszewski (*Chem. Zentr.*, 1910, ii, 1048; from *Kosmos*, 1910, **35**, *Radziszewski-Festband*, 538—542).—The solubility of sodium picrate in aqueous solutions of sodium, carbonate, chloride, sulphate, phosphate, nitrate, bromide, and hydroxide of various strengths at 25° was determined. The measurements have proved that, contrary to the statement of Reinhard (*Zeitsch. anal. Chem.*, 1910, **49**, 269), the solubility of sodium picrate is lowered by the presence of the sodium ions in accordance with the law of mass action. N. C.

New Derivatives of Indene. Victor Grignard and Charles Courtot (*Compt. rend.*, 1911, **152**, 272—274).—Organo-magnesium bromides act on indene, giving rise to a sparingly soluble *magnesium indenyl bromide*, $CH{<}\substack{C_6H_4\\CH}{>}CH\cdot MgBr$. When treated in the usual way, this yields the two following compounds: 1-*Indenol*, C_9H_8O, yellow prisms, m. p. 57—58°, b. p. 140°/10 mm., with partial dehydration. *Indene-1-carboxylic acid*, $CH{<}\substack{C_6H_4\\CH}{>}CH\cdot CO_2H$, chamois-coloured, prismatic needles, m. p. 161°.

Magnesium indenyl bromide reacts with fluorenone at 120° to give a theoretical yield of tert.-1-*indenylfluorenol* (I):

$$\begin{array}{l} CH\cdot C_6H_4 \quad C_6H_4 \\ \| \qquad\;\; | \\ CH\cdot CH\text{——}C(OH) \end{array}{>}C_6H_4 \qquad\qquad \begin{array}{l} CH\cdot C_6H_4 \\ \| \qquad\;\; | \\ CH\cdot CH\cdot CPh_2\cdot OH \end{array}.$$

(I.) (II.)

This compound crystallises in colourless needles, m. p. 151—152°. In the same way, benzophenone gives 1-*indenyldiphenylcarbinol* (II), a substance occurring in pale yellow tablets, m. p. 131—132°. A portion of the carbinol undergoes dehydration during the preparation, forming *diphenylbenzfulvene*, $CH{<}\substack{C_6H_4\\CH}{>}C{:}CPh_2$, orange-yellow spangles, m. p. 111—112°. W. O. W.

Anthracene. I. Anthranol and Anthraquinol. Kurt H. Meyer (*Annalen*, 1911, **379**, 37—73).—Dimroth's dianthrone and

Meyer's dianthranol (Abstr., 1909, i, 168), which are stable separately, not only in the solid state, but also in solution, and are mutually interconvertible only by energetic chemical means, are distinct isomerides, not tautomerides of the enol-keto-type, claimed by Thiele and by Baly for phenols of the benzene series. In the present paper the author shows that the monohydric and dihydric meso-phenols of the anthracene series, anthranol and anthraquinol, can each exist in two stable desmotropic forms.

The substance, long known as anthranol, reacts sometimes as a phenol, sometimes as a ketone; it is colourless, completely insoluble in cold aqueous alkalis, and its solutions generally are non-fluorescent. When its 5—10% solution in boiling sodium hydroxide is cooled rapidly to $-5°$ and treated with cold 5% sulphuric acid, a new *substance*, $C_{14}H_{10}O$, is obtained, which crystallises in brownish-yellow leaflets, is easily soluble in cold aqueous alkalis, and forms solutions with an intense blue fluorescence; it sinters at 120° and melts completely at about 152°, but when placed in a bath previously heated to 120°, it melts at once. This substance is called anthranol, the name anthrone being reserved for the older substance. Anthranol changes into anthrone by keeping in a desiccator. The two substances attain a state of equilibrium when fused or dissolved, the change being easily followed by the formation or the disappearance of the blue fluorescence. Since both substances separately are stable for a long time in alcohol, it is possible to answer the question whether the activity of phenols is due to the enolic or to the keto-modification. In cold alcohol anthrone is not attacked by iodine, bromine, ferric chloride, or amyl nitrite; on boiling, however, particularly in solvents which cause a rapid transformation of anthrone into anthranol, reactions occur. In cold alcohol anthranol is attacked at once by bromine or iodine, and is oxidised to dianthrone by ferric chloride; also amyl nitrite in benzene at the ordinary temperature oxidises anthranol to dianthrone; dianthranol is never produced, not even when anthranol is oxidised by alkaline potassium ferricyanide. An alcoholic solution of anthranol at 25° couples readily with *p*-nitro*anti*diazobenzene hydrate to form Kaufler and Suchannek's anthraquinone-*p*-nitrophenylhydrazone; under similar conditions anthrone does not couple; also nitrosodimethylaniline condenses with anthranol, but not with anthrone, in alcoholic solution. Thus the reactivity of the hydroxylic modification supports Dimroth's results in connexion with the reactivity of enol-keto-tautomerides in the aliphatic series (Abstr., 1907, i, 662).

As is well known, anthraquinol (oxanthranol), obtained by reducing anthraquinone with zinc dust and alkali, forms brown leaflets, dissolves in cold aqueous sodium hydroxide to form a red disodium salt, yields solutions with an intense green fluorescence, and is rapidly oxidised to anthraquinone by iodine, bromine, or oxygen; its *dibenzoate* has m. p. 292°, and is non-fluorescent. Consequently oxanthranol is the true anthraquinol, $C_6H_4<\begin{matrix}C(OH)\\|\\C(OH)\end{matrix}>C_6H_4$. It cannot be readily transformed into the keto-modification, *oxanthrone*,

$C_6H_4<\begin{matrix}-CO-\\CH(OH)\end{matrix}>C_6H_4$, which is readily obtained; however, by hydrolysing bromoanthrone (Goldmann's bromoanthranol) by boiling 50% aqueous acetone (see also following abstract). Oxanthrone, m. p. 167°, forms yellow, almost colourless needles, gives colourless solutions which are non-fluorescent and are not attacked by oxygen, iodine, or bromine in the cold, is easily reduced to anthranol by zinc dust and acetic acid (anthraquinol is not reduced), and is unchanged by cold aqueous alkalis. Boiling alkalis convert oxanthrone into anthraquinol. The two substances can be fused without changing the one into the other. Also, in boiling solvents they are for the most part unchanged; the addition of a catalyst, however, such as hydrogen chloride or sodium acetate, to the alcoholic solutions causes an almost complete change of the oxanthrone into anthraquinol. *Oxanthrone acetate*, $C_6H_4<\begin{matrix}-CO-\\CH(OAc)\end{matrix}>C_6H_4$, m. p. 108°, is obtained from bromoanthrone and potassium acetate in hot glacial acetic acid; the action of acetyl chloride on oxanthrone in pyridine yields Liebermann's anthraquinyl diacetate.

Meisenheimer's methoxyanthrone, $C_6H_4<\begin{matrix}-CO-\\CH(OMe)\end{matrix}>C_6H_4$, obtained by boiling bromoanthrone with methyl alcohol, is partly converted by boiling alcohol and hydrochloric acid or by luke-warm dilute sodium hydroxide into *anthraquinyl methyl ether*,

$$C_6H_4<\begin{matrix}C(OH)-\\|\\C(OMe)\end{matrix}>C_6H_4,$$

m. p. 164°, which is also obtained by shaking an alkaline solution of anthraquinol with methyl sulphate, filtering in hydrogen, and extracting the filtrate with ether in an atmosphere of carbon dioxide. The ether forms an *acetate*, m. p. 174°, and a *benzoate*, m. p. 224°, separates in stout, brown crystals, yields solutions with a bluish-green fluorescence, and dissolves in cold alkalis, forming reddish-yellow solutions which are easily oxidised by iodine, bromine, or oxygen to anthraquinone and 9 : 9′-*dimethoxydianthrone*,

$$CO<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C(OMe)\cdot C(OMe)<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CO,$$

m. p. 239–240°. *Anthraquinyl dimethyl ether*,

$$C_6H_4<\begin{matrix}C(OMe)\\|\\C(OMe)\end{matrix}>C_6H_4,$$

m. p. 202°, obtained as a by-product in the reaction between anthraquinol and methyl sulphate, forms colourless plates with a blue fluorescence; its solutions also are fluorescent, and are not attacked by iodine or bromine in the cold. *Anthraquinyl diethyl ether*, m. p. 148°, obtained from anthraquinol and ethyl sulphate and purified by means of 80% alcohol, forms colourless needles with a blue fluorescence; its solution in chloroform or carbon disulphide is decolorised by bromine, anthraquinone being formed. The alcoholic mother-liquor contains Liebermann's ethyloxanthrone, m. p. 107°.

By a consideration of the distribution of the residual affinity, Meisenheimer has shown that addition takes place at the *meso*-carbon

atoms in derivatives of anthracene, and at the oxygen atom in those of anthrone and anthraquinone. The author shows that this theory is applicable, not only to explain, but also to predict, the preceding results. C. S.

Anthracene. II. Oxidation of Anthracene. KURT H. MEYER (*Annalen*, 1911, **379**, 73—78. Compare preceding abstract).—Most oxidising agents which attack anthracene convert it into anthraquinone. By using lead dioxide and glacial acetic acid, Schulze obtained a substance which was supposed to be different from anthraquinol (oxanthranol), and was called β-oxanthranol. It is, however, anthraquinol itself, produced, as the sequel shows, from the initially-formed oxanthrone acetate by the boiling alkali used by Schulze in the process of purification.

By oxidising anthracene in glacial acetic acid at 50° by lead dioxide (1 mol.), the author obtains 40—50% of anthranyl acetate, together with a little oxanthrone acetate and anthraquinone. When the oxidation is effected at 70° by 2 mols. of lead dioxide, the main product is oxanthrone acetate.

The oxidation of anthracene by manganese dioxide, cerium acetate, or vanadic acid proceeds in a similar manner, provided that glacial acetic acid is used as the solvent; a solution of anthracene in alcohol and toluene is oxidised by manganese dioxide and a drop of sulphuric acid to viscous products, amongst which occurs dianthrone.

Anthracene is oxidised very smoothly to oxanthrone by bromine in aqueous acetone, only a trace of anthraquinone being formed; the action of chlorine on an aqueous suspension of anthracene is similar, but less satisfactory, as regards purity of product. By allowing solutions of anthracene in glacial acetic acid and of bromine in methyl alcohol to flow simultaneously into a large volume of methyl alcohol, methoxyanthrone together with a little anthraquinone and unchanged anthracene are produced. C. S.

***p*-Xylyl Sulphide and its Derivatives.** Z. MARTYNOWICZ (*Chem. Zentr.*, 1910, ii, 1048; from *Kosmos*, 1910, **35**, *Radziszewski-Festband*, 594—596).—p-*Xylyl sulphide*, $S(CH_2\cdot C_6H_4Me)_2$, obtained by the action of an alcoholic solution of potassium sulphide on *p*-xylyl bromide, forms colourless needles, m. p. 76°. By oxidation with nitric acid, it forms p-*xylylsulphoxide*, $SO(CH_2\cdot C_6H_4Me)_2$, which crystallises in silky needles, m. p. 117°. Both these substances form on oxidation with potassium permanganate, p-*xylylsulphone*, $SO_2(CH_2\cdot C_6H_4Me)_2$, which forms shining plates, m. p. 197°. N. C.

The Action of Ammonia on Aromatic Thiocyanates. MARYA STRZELECKA (*Chem. Zentr.*, 1910, ii, 1135; from *Kosmos*, 1910, **35**, *Radziszewski-Festband*, 585—589).—When aromatic thiocyanates are boiled for a long time with alcoholic ammonia, ammonium cyanide is split off with the formation of disulphides. In this way the following disulphides were prepared: benzyl disulphide, $(CH_2Ph)_2$, white crystals, m. p. 71—72°; p-*xylyl disulphide*, white radiating tufts of needles, m. p. 43°; o-*xylyl disulphide*, white plates, m. p. 83—85°. The *meta*-compound could not be obtained in this way. N. C.

Phenyl Thiocarbonate. Angelo Casolari (*Gazzetta*, 1910, **40**, ii, 389—402).—Potassium trithiocarbonate reacts with diazobenzene chloride in aqueous solution with formation of *phenyl trithiocarbonate*, CS_3Ph_2, which is a red oil, D_4^0 1·2668, $D_4^{19·5}$ 1·2497. It has the normal molecular weight. Heat decomposes the substance somewhat readily, with formation of hydrogen sulphide and carbon disulphide among other products. When subjected to distillation, the compound evolves vapour at 210—215°/30 mm., and the distillate consists of phenyl disulphide. The action of alcoholic potassium hydroxide, alcoholic ammonia, or aqueous ammonia in a sealed tube, leads to the production of thiophenol, carbon disulphide, a carbonate, and a thiosulphate. As secondary products from the carbon disulphide are formed thiocyanic acid and hydrogen sulphide (when ammonia is used) and xanthic acid (with alcoholic potassium hydroxide).

Thiosulphates give a characteristic blue coloration when treated with a few drops of a 5% solution of sodium nitroprusside which has been exposed to light and air until it has assumed a chestnut-brown colour. The coloration is green in very dilute solutions; it is stable in neutral solutions or in the presence of potassium hydrogen tartrate, but becomes green and finally yellow in the presence of alkali, acid, or oxidisers. The reaction is not given by sulphites or by tetrathionates. The reagent may also be made by treating a fresh solution of sodium nitroprusside with potassium ferricyanide, then with potassium hydroxide, and finally rendering the liquid just acid with potassium hydrogen tartrate. R. V. S.

Sulphur Derivatives of *o*-Cresol. Theodor Zincke and R. Brune (*Ber.*, 1911, **44**, 185—197. Compare Zincke and Glahn, Abstr., 1907, i, 698).—3-*Bromo*-o-*cresol*-5-*sulphonyl chloride*,

$$OH·C_6H_2BrMe·SO_2Cl,$$

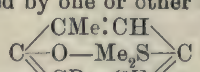
prepared by the action of phosphoryl chloride on potassium bromo-*o*-cresol-sulphonate (Claus and Jackson, Abstr., 1889, 129) at 150°, crystallises from light petroleum in colourless needles, m. p. 94°, and yields an *acetyl* derivative in the form of colourless prisms, m. p. 131°. The *methyl* ester, $OH·C_6H_2MeBr·SO_2Me$, forms colourless plates, m. p. 141—142°; the *ethyl* ester, compact needles, m. p. 113°, and the *anilide*, minute crystals, m. p. 165—166°. Potassium acetate reacts with an acetone solution of the chloride, yielding a polymeric *bromosulphonyl*-p-*toluquinone*, $\left[SO_2{:}C{<}\begin{matrix}CH{:}CMe\\CH{=}CBr\end{matrix}{>}C{:}O\right]_n$, which crystallises from nitrobenzene in small, colourless needles, with no definite m. p. 3-*Bromo*-5-*thiol*-o-*cresol*, $SH·C_6H_2MeBr·OH$, obtained by reducing the sulphonyl chloride with zinc dust, alcohol, and hydrochloric acid, crystallises from light petroleum in colourless needles, m. p. 51—52°. The *diacetyl* derivative, $C_{11}H_{11}O_3SBr$, forms small, compact plates, m. p. 111—112°. Concentrated ferric chloride solution oxidises the thiol in the presence of glacial acetic acid to 3-*bromo*-o-*cresol* 5-*disulphide*, $S_2(C_6H_2BrMe·OH)_2$, which crystallises from light petroleum in thick, yellow plates, m. p. 123—124°. The corresponding *acetyl* derivative, $C_{18}H_{16}O_4S_2Br_2$, forms colourless plates,

m. p. 101—102°, and is also formed when the thiol is warmed with acetic anhydride and a little sulphuric acid.

3-*Bromo*-5-*methylthiol*-o-*cresol*, $OH\cdot C_6H_2MeBr\cdot SMe$, obtained by methylating the thiol with methyl iodide and sodium methoxide in the cold, is a colourless oil, b. p. 167—169°/20—21 mm., and yields an *acetyl* derivative, $C_{10}H_{11}O_2SBr$, in the form of glistening, rhombic plates, m. p. 53°. When shaken with water the methyl sulphide yields a yellow, amorphous powder, $C_{32}H_{33}O_4S_4Br$, m. p. about 90° after sintering at 50—60°. Dilute alkali hydroxide solutions react in much the same manner as water. Sodium nitrite reacts with a glacial acetic acid solution of the methyl sulphide, yielding 3-*nitro*-5-*methylthiol*-o-*cresol*, $SMe\cdot C_6H_2Me(NO_2)\cdot OH$, which crystallises in orange-red needles, m. p. 78—79°; its *acetyl* derivative forms yellow needles, m. p. 70°. 3-*Bromo*-o-*cresol* 5-*methylsulphoxide*, $OH\cdot C_6H_2MeBr\cdot SOMe$, obtained by oxidising a glacial acetic acid solution of the methyl sulphide with hydrogen peroxide, crystallises from benzene in well-developed, colourless needles, m. p. 121°; it dissolves in alkalis without decomposition, and yields a perbromide. The corresponding *sulphone*, $OH\cdot C_6H_2MeBr\cdot SO_2Me$, obtained by using excess of hydrogen peroxide, crystallises in colourless needles or prisms, m. p. 168°. 3 : 6-*Dibromo*-5-*methylthiol*-o-*cresol perbromide*, $OH\cdot C_6HMeBr_2\cdot SMeBr_2$, exists in two modifications, namely, orange-red plates from acetic acid and brownish-violet needles from chloroform. Both forms lose bromine, yielding 3 : 6-*dibromo*-5-*methylthiol*-o-*cresol*, $C_8H_8OSBr_2$, which crystallises from light petroleum in colourless needles or rhombic plates, m. p. 111—112°. 3 : 6-*Dibromo*-o-*cresol*-5-*methylsulphoxide*, $OH\cdot C_6HMeBr_2\cdot SMeO$, prepared by the action of water on the perbromide, crystallises from benzene in stout, colourless needles, m. p. 168°, and the corresponding *sulphone*, $C_8H_8O_3SBr_2$, forms colourless needles, m. p. 169°.

3-*Bromo*-o-*cresol*-5-*dimethylsulphinium iodide*, $OH\cdot C_6H_2MeBr\cdot SMe_2I$, prepared by the action of methyl iodide on the thiol derivative in the presence of an excess of alkali, crystallises in felted needles, m. p. 114° (decomp.). The corresponding *chloride*, $C_9H_{12}OSClBr$, forms slender needles, m. p. 151° (decomp.), and the *platinichloride* crystallises in brownish-yellow needles.

The *anhydro*-compound, $C_9H_{11}OSBr$, obtained by the action of moist silver oxide on the sulphinium iodide, crystallises in colourless needles, m. p. 185—187°, after darkening at 170°. It must be represented by one or other of the formulæ:

 or $O{:}C{<}\begin{matrix}CMe{:}CH\\CBr{:}CH\end{matrix}{>}C{:}SMe_2$.

The corresponding *nitrothionium quinone*,

$$O{:}C{<}\begin{matrix}CMe{=}CH\\C(NO_2){:}CH\end{matrix}{>}C{:}SMe_2,$$

crystallises in glistening, yellow needles, m. p. 245—246°, and when boiled for some time with dilute alkalis yields the nitromethylthiolcresol. The *nitrate*, $C_9H_{11}O_3NS,HNO_3$, forms stout, yellow prisms, m. p. 150—151° (decomp.); the *chloride* forms pale yellow plates, m. p. 99—100° (decomp.), and the *platinichloride*, $2C_9H_{11}O_3NS,H_2PtCl_6$, forms compact, yellow needles. J. J. S.

Action of Magnesium Phenyl Bromide on Heptaldehyde. U. Colacicchi (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 600—605).—*Phenylhexylcarbinol*, $C_{13}H_{20}O$ (from magnesium phenyl bromide and heptaldehyde), is a colourless liquid, b. p. 156°/25 mm., 176°/40 mm., or 275° at the ordinary pressure, D 0·9455, n (yellow) 1·501. Its *phenylurethane*, $C_{20}H_{25}O_2N$, forms rosettes of colourless crystals, m. p. 77°. The *phenylthiourethane* crystallises in laminæ, m. p. 147°. Phenylhexylcarbinol, when reduced with iodine and phosphorus, yields the corresponding *iodide*, which is a liquid, b. p. 140°/38 mm., and a *substance* (probably a hydrocarbon) distilling at 290—360°. By oxidation of the carbinol, phenyl hexyl ketone is obtained, identical with that described by Auger (Abstr., 1887, 814). The *semicarbazone* of the ketone, $C_{14}H_{21}ON_3$, forms colourless needles, m. p. 118—119°. The p-*nitrophenylhydrazone*, $C_{19}H_{23}O_2N_3$, crystallises in yellow needles, m. p. 127—128°.

Experiments on the physiological action of the compounds described show that the toxicity of the alcohol is somewhat greater than that of the ketone, both for warm-blooded (*Mus musculus*) and cold-blooded (*Rana esculenta*) animals. Both substances eventually cause paralysis of the central nervous system, and diminish the amplitude of the beats of the heart, which finally stops in diastole. R. V. S.

Dextrorotatory Phytosterols of Anthemis nobilis (Anthesterols). Timothée Klobb (*Compt. rend.*, 1911, **152**, 327—330. Compare Abstr., 1909, i, 471).—The existence of isomeric benzoates and the variable composition of its bromo-derivatives suggest that anthesterol is not a single substance. To throw light on this point, the alcohol was treated with acetic anhydride, when three isomeric acetates were obtained. A. Hexagonal lamellæ, m. p. 245—248°, $[\alpha]_D$ +91·2°; this yields α-anthesterol on hydrolysis. B. Hexagonal lamellæ, m. p. 225—230°, $[\alpha]_D$ +73·9°; β-anthesterol is obtained on hydrolysis. (C) Confused crystals, m. p. 185—195°, giving on hydrolysis needles having a double m. p., 158—160° and 185—190°.

On bromination the acetate, (A) yields two *monobromo*-derivatives, $C_{31}H_{50}OBrAc$, m. p. about 180°, but having $[\alpha]_D$ +133° and +58·8° respectively. (B) gives a *dibromo*-additive product, $C_{31}H_{51}OBr_2Ac$, m. p. 170—175°. (C) forms a mixture of the bromo-acetate from (A), with a substance corresponding in composition with a mixture of the (A) and (B) bromo-derivatives containing 45% of the latter.

The interpretation placed on these results is that anthesterol has the formula $C_{31}H_{52}O,3H_2O$, and is an individual substance homologous with amyrin and paltreubin (Jungfleisch and Leroux, Abstr., 1906, i, 525; 1907, i, 783; 1908, i, 1000). It is not identical with lupeol as suggested by Cohen (Abstr., 1908, i, 882). W. O. W.

Esterification of Benzamide and the Preparation of *N*-Substituted Benzamides. E. Emmet Reid (*Amer. Chem. J.*, 1911, **45**, 38—47).—Bonz (Abstr., 1889, 335) made a study of the reversible reaction: $CH_3{\cdot}CO{\cdot}NH_2 + EtOH \rightleftarrows CH_3{\cdot}CO_2Et + NH_3$, and identified ethylamine among the reaction products. He assumed that the amine was produced by the action of ammonia on the ester previously formed,

thus: $CH_3\cdot CO_2Et + NH_3 = CH_3\cdot CO_2\cdot NH_3Et$, but his results are more simply accounted for by supposing that the amide and alcohol react directly to form acetoethylamide:

$$CH_3\cdot CO\cdot NH_2 + EtOH = CH_3\cdot CO\cdot NHEt + H_2O.$$

In connexion with certain other work (Abstr., 1910, i, 481, 701), the author studied the action of alcohol on benzamide and found that benzoethylamide could be readily obtained. The work has been continued and extended to other alcohols. The reactions which take place when ethyl alcohol is heated with benzamide are as follows: $C_6H_5\cdot CO\cdot NH_2 + EtOH \rightleftharpoons C_6H_5\cdot CO_2Et + NH_3$, $C_6H_5\cdot CO\cdot NH_2 + EtOH = C_6H_5\cdot CO\cdot NHEt + H_2O$. The benzoethylamide undergoes hydrolysis according to the reaction:

$$C_6H_5\cdot CO\cdot NHEt + H_2O \rightleftharpoons C_6H_5\cdot CO_2H,NH_2Et,$$

which finally reaches equilibrium.

Benzamide was heated with a slight excess of the alcohol in a sealed tube at 220—230° for periods varying from two to seven days. In an experiment with methyl alcohol, 39% of benzomethylamide was isolated, but no methyl benzoate was obtained, and 61% of the amide underwent hydrolysis. In two experiments with ethyl alcohol, the yields of benzoethylamide were 61·1 and 62·6%, of ethyl benzoate 1·27 and 1·58%, whilst the amounts of amide hydrolysed were 38·1 and 36·4%. With propyl alcohol the yield of benzopropylamide was 72·9%, of propyl benzoate 5·2%, and the amide hydrolysed amounted to 23·1%. In the case of *iso*butyl alcohol, 69·4% of benzo*iso*butylamide was obtained and 8·3% of *iso*butyl benzoate, whilst 24·3% of the amide suffered hydrolysis.

The amount of benzamide transformed into the ester seems to increase with the molecular weight of the alcohol. In the case of the experiment with methyl alcohol, a small quantity of water was present, and a large amount of hydrolysis therefore occurred.

The action of alcohols on benzamide affords a convenient method for preparing certain benzoalkylamides, and may also be of service for the preparation of the amines which are obtained as by-products.

E. G.

Study of *o*-Amino-*p*-sulphobenzoic Acid with Special Reference to its Fluorescence. JOSEPH H. KASTLE (*Amer. Chem. J.*, 1911, **45**, 58—78).—Aqueous solutions of *p*-aminobenzoic sulphinide exhibit a bluish-purple fluorescence, but solutions in concentrated hydrochloric acid are not fluorescent. Since several difficulties arise in attempting to elucidate the causes of this phenomenon, the author has studied *o*-amino-*p*-sulphobenzoic acid (Hart, Abstr., 1881, 1146), which, on account of its simpler constitution, appeared more suitable for an investigation of the influence of simple chemical changes on fluorescence.

o-Amino-*p*-sulphobenzoic acid crystallises with $\frac{1}{2}H_2O$, and in dilute aqueous solution exhibits a bluish-purple fluorescence which, within certain wide limits, is inversely proportional to the concentration. The intensity of the fluorescence of both the acid and its salts is diminished by heat. The fluorescence of aqueous solutions of the acid is weakened or destroyed by strong acids and alkalis, the power of

effecting this change being roughly proportional to the degree of ionisation of the reagent. The intensity of the fluorescence of sodium, potassium, ammonium, calcium, barium, and magnesium *o*-amino-*p*-sulphobenzoates is independent of the nature of the base. Solutions of the acid and of the acid salts are much more fluorescent than those of the normal salts, whilst the fluorescence of solutions of the acid salts is somewhat more intense than that of solutions of the free acid.

Di-silver o-*amino*-p-*sulphobenzoate* exists in two forms, one amorphous and unstable above 27·5°, the other crystalline, stable at 27·5° and at higher temperatures, and less soluble in water than the amorphous variety. By the action of ethyl iodide on the crystalline di-silver salt, a compound, probably o-*ethylamino*-p-*sulphobenzoic acid*, $CO_2H{\cdot}C_6H_3(NHEt){\cdot}SO_3H,H_2O$, m. p. 243° (decomp.), is produced, which forms colourless, rhombic crystals, and exhibits a blue fluorescence in dilute aqueous solution. In one experiment, another *compound*, m. p. 160°, probably either the true diethyl ester or the acid ester of the ethylamino-acid, $CO_2Et{\cdot}C_6H_3(NHEt){\cdot}SO_3H$, was obtained, which forms pale yellow crystals, and, when boiled with water, is converted into the substance melting at 243°. A *barium* salt, probably $[CO_2Et{\cdot}C_6H_3(NHEt){\cdot}SO_3]_2Ba$, has also been prepared.

E. G.

Iminosulphides. I. The Condensation of Thiobenzamide with Benzonitrile. MOTOOKI MATSUI (*Mem. Coll. Sci. Eng. Kyoto*, 1910, 2, 401—404).—Under the influence of hydrochloric acid, thiamides combine with nitriles to form iminosulphides of the constitution: $S(CR{:}NH)_2$.

Benziminosulphide, $S(CPh{:}NH)_2$, obtained in the form of its hydrochloride by the action of hydrochloric acid on an ethereal solution of thiobenzamide and benzonitrile, crystallises in light red needles, m. p. 71°; the *acetyl* derivative crystallises in orange needles, The *hydrochloride*, $C_{14}H_{12}NS,2HCl$, forms orange needles, m. p. 110—111°, and is decomposed by water, yielding the free base. The *picrate*, $C_{14}H_{12}NS,C_6H_3O_7N$, crystallises in light red, prismatic plates, containing one molecule of alcohol; when heated at 80°, the alcohol of crystallisation is lost, and the picrate is obtained as an amorphous, yellow substance, m. p. 114°.

F. B.

Degradation of Amino-acids by Fermentation with Yeast. OTTO NEUBAUER and KONRAD FROMHERZ (*Zeitsch. physiol. Chem.*, 1911, 70, 326—350. Compare Abstr., 1909, ii, 750).—Stress is laid on the possible analogy between the conversion of an amino-acid into alcohol by means of yeast and into fatty-acid in the mammalian organism. In each case it is considered that the ketonic acid $R{\cdot}CO{\cdot}CO_2H$ is the intermediate product.

It is shown that by the action of yeast on α-aminophenylacetic acid, benzoyl alcohol, phenylglyoxylic acid, *l*-mandelic acid, and *l*-acetyl aminophenylacetic acid are formed. Yeast is able to effect a partial reduction of phenylglyoxylic acid to *l*-mandelic acid. The ketonic acid, *p*-hydroxylphenylpyruvic acid, is converted by yeast to a large extent

into *p*-hydroxyphenylethyl alcohol. *p*-Hydroxyphenyl-*a*-lactic acid, on the other hand, is not converted to any extent into *p*-hydroxyphenylethyl alcohol, proving that this alcohol acid is not the intermediate product between keto-acid and alcohol. The conversion of amino-acid into alcohol involves a series of alternate oxidative and reducing changes.

E. F. A.

Transformation of δ-Phenyl-Δ^a-pentenoic Acid into the Δ^γ-Isomeride. J. BOUGAULT (*Compt. rend.*, 1911, **152**, 196—197).—Fittig (Abstr., 1895, ii, 204) has shown that *β*-hydroxyvaleric acid is formed on boiling δ-phenyl-Δ^a-pentenoic acid with aqueous alkalis, together with a substance which he supposed to be δ-phenyl-Δ^β-pentenoic acid. The present author has been unable to obtain the latter substance, but finds that the Δ^γ-acid is an important product of the transformation, under the most favourable conditions the yield amounting to 50%. The formation of *β*-hydroxyvaleric acid was confirmed. An acidic liquid, possibly a mixture, is also produced in small quantity.

W. O. W.

Introduction of the Carboxylic Group into Polynuclear Aromatic Hydrocarbons. CARL LIEBERMANN and M. ZSUFFA (*Ber.*, 1911, **44**, 202—210).—The methods of Graebe and Liebermann (*Ber.*, 1869, **2**, 678), Friedel and Crafts (this Journ., 1877, ii, 725), and Gattermann (Abstr., 1888, 574) for the introduction of the carboxylic group into polynuclear aromatic hydrocarbons give but poor yields, and in many cases do not work. The authors have prepared the following acids by treating the corresponding hydrocarbons with 2·5 times their weight of oxalyl chloride at 160—170°, and extracting with cold sodium carbonate solution; the numbers indicate the percentage yields: anthracene-9-carboxylic acid, m. p. 217° (70—80%); fluorenecarboxylic acid (this Journ., 1877, ii, 493) (7—10%); indenecarboxylic acid, by using a temperature of 140—145° (15%), m. p. 234° (compare Perkin and Révay, Trans., 1893, **65**, 238); acenaphthenecarboxylic acid, also obtained by heating at 180° for fourteen hours (30%) (compare Gattermann, Abstr., 1888, 574); phenanthrene-9-carboxylic acid (yield poor); chrysenecarboxylic acid, by heating for two days at 170°, yield poor.

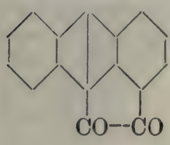
Better yields are obtained when aluminium chloride is added to the hydrocarbon and oxalyl chloride. The mixture becomes quite black even when carbon disulphide is present, but on adding water, the colour changes to yellow or red. The yields are better, but the products less pure.

Naphthalene gives a mixture of 80% of *a*- and *β*-naphthoic acids, and anthracene yields anthracene-9-carboxylic acid (30%) and aceanthrenequinone (60%).

Benzene and naphthalene are not carboxylated in the absence of aluminium chloride, and when anthracene is heated with excess of oxalyl chloride at 200°, 10-chloroanthracene-9-carboxylic acid is formed (70%) (compare Behla, Abstr., 1886, 248; 1887, 593).

Chrysenecarboxylic acid, $C_{18}H_{11}\cdot CO_2H$, crystallises from alcohol in colourless needles, m. p. 303°, and the *sodium* salt, $C_{19}H_{11}O_2Na$, crystallises from water in long plates.

Aceanthrenequinone (annexed formula) crystallises from benzene in brilliant red prisms, m. p. 270°, and when sublimed has the appearance of alizarin. It combines with sodium hydrogen sulphite, is oxidised by chromic acid to anthraquinonecarboxylic acid, and an acetic acid solution reacts with an alcoholic solution of *o*-toluylenediamine, yielding *aceanthrenetolazin*,



$$C_{14}H_8<\begin{matrix}C{:}N\\ |\\ C{:}N\end{matrix}>C_6H_3Me.$$

This crystallises in orange-red needles or plates, m. p. 237°, and its alcoholic solution has a green fluorescence. J. J. S.

Preparation of 3 : 5-Di-iodotyrosine from Iodoprotein. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, **70**, 310—313).—3 : 5-Di-iodotyrosine has been isolated among the products of the hydrolysis of iodo-albacid with barium hydroxide (Blum and Vaubel, Abstr., 1898, i, 610). It is suggested that iodine is, in part, attached to tyrosine in the natural iodoproteins. E. F. A.

Conversion of Coumarins into Coumarinic Acids and *o*-Coumaric Acids. II. KARL FRIES and W. VOLK (*Annalen*, 1911, **379**, 90—110. Compare Abstr., 1908, i, 820).—Experiments similar to those already recorded (*loc. cit.*) have been performed on 4-methylcoumarin, 3-methylcoumarin, and 3-ethylcoumarin.

The conversion of 4-methylcoumarin into β-methylcoumarinates by aqueous alkalis is slower than that of coumarin into a coumarinate, but, conversely, its conversion by concentrated alkali into *β-methyl-o-coumaric acid*, $OH\cdot C_6H_4\cdot CMe{:}CH\cdot CO_2H$, m. p. 154° (decomp.), proceeds more readily (five hours' boiling with 33% potassium hydroxide) than that of coumarin into *o*-coumaric acid. When 4-methylcoumarin is heated with alcoholic potassium ethoxide at 140—150° for fifteen hours and the product is acidified, 1-(2-*methylcoumaran*)-3-(4-*methylcoumarin*) *ketone* (3-[2-*methylhydrocoumarilyl*]-4-*methylcoumarin*), $C_{20}H_{16}O_4$, m. p. 224°, is obtained, the constitution and behaviour of which are similar to those of the ketone obtained in the same manner from 4 : 7-dimethylcoumarin (*loc. cit.*); when boiled for a short time with dilute aqueous alkali, it loses carbon dioxide and yields *di*-1-(2-*methylcoumaran*) *ketone* (1-[2-*methylhydrocoumarilyl*]-2-*methylhydrocoumarone*), $\left(C_6H_4<\begin{matrix}CHMe\\ O\end{matrix}>CH\right)_2CO$, m. p. 183—185°, solidifying to a glassy mass which has m. p. about 95°, re-solidifies at about 145°, and melts again at 184°. This substance forms yellow solutions in alkalis, and yields an *oxime*, m. p. 213°.

3-Methyl-(or ethyl-)coumarin behaves towards aqueous alkalis and sodium ethoxide like those coumarins which are not alkylated in the pyrone nucleus. After being boiled for five hours with 33% potassium hydroxide, only salts of the alkylcoumarinic acid are formed, since carbon dioxide causes the precipitation of the 3-alkylcoumarin. When boiled for five hours with alcoholic sodium ethoxide, however, the 3-alkylcoumarins yield salts of the α-alkyl-*o*-coumaric acids, although more slowly than is the case with coumarin and its *Bz*-homologues.

a-Methyl-o-coumaric acid, $OH\cdot C_6H_4\cdot CH\colon CMe\cdot CO_2H$, m. p. 138° (decomp.), and *a-ethyl-o-coumaric acid*, m. p. 181° (decomp.), form yellow solutions in concentrated sulphuric acid, yield alkali salts which exhibit a yellowish-green fluorescence in solution (the alkali salts of β-alkyl-*o*-coumaric acids do not show fluorescence), and are not reconverted into the 3-alkylcoumarins very smoothly, in this respect resembling *o*-coumaric acid, but differing from β-alkyl-*o*-coumaric acids.

The replacement by methyl groups of hydrogen atoms in the benzene nucleus of coumarins does not affect greatly the behaviour of the resulting alkylcoumarins, except in so far as slight variations in the velocity of formation of the *o*-coumaric acids are concerned. It is very striking, therefore, that the introduction of hydroxy-, methoxy-, or dimethylamino-groups in the *Bz*-nucleus prevents completely the formation of the corresponding *o*-coumaric acids; thus 4-methylumbelliferone, its methyl ether, and 7-dimethylamino-4-methylcoumarin are only converted into the corresponding coumarinates even after prolonged boiling with alcoholic sodium ethoxide or concentrated aqueous potassium hydroxide. 7-Dimethylamino-4-methylcoumarin is decomposed completely by boiling for six hours with 40% potassium hydroxide, *m*-dimethylaminophenol being formed.

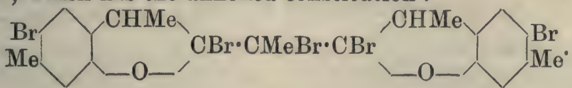
7-Methylcoumarin-4-acetic acid, $C_6H_3Me{<}{\begin{matrix}C(CH_2\cdot CO_2H)\\ \text{———}O\cdot CO\text{———}\end{matrix}}{>}CH$, m. p. 190° (decomp.; thereby yielding 4:7-dimethylcoumarin), obtained together with its ethyl and *m*-tolyl esters by the interaction of *m*-cresol, ethyl acetonedicarboxylate, and concentrated sulphuric acid at 0°, does not behave like 4-methylcoumarin; with aqueous alkalis it does not form an *o*-coumarate, and with alcoholic sodium ethoxide a ketone is not produced, in both cases a coumarinate being formed which is easily reconverted into the coumarin by acids. The *ethyl* ester, $C_{14}H_{14}O_4$, m. p. 132°, behaves in a similar manner, being hydrolysed by aqueous alkalis and yielding a coumarinate with sodium ethoxide. The m-*tolyl* ester, $C_{19}H_{16}O_4$, m. p. 214°, however, behaves differently. By prolonged boiling with 20% potassium hydroxide, it is partly hydrolysed, partly unchanged, and partly converted into the following *o*-coumaric acid and a substance which yields 2:2:4:6-tetrabromo-3-keto-2:3-dihydrotoluene (Foster, Dissert., Marburg, 1898) by treatment with bromine. By treatment with alcoholic potassium ethoxide at 130—140° for fifteen hours, the *m*-tolyl ester yields, after acidifying the product, the m-*tolyl* ester of *a-acetic-4-methyl-o-coumaric acid*,

$$OH\cdot C_6H_3Me\cdot C(CH_2\cdot CO_2\cdot C_6H_4Me)\colon CH\cdot CO_2H,$$

which sinters at 95°, melts and decomposes at about 100°, resolidifies at about 120°, and melts again at 214°, the m. p. of the corresponding coumarin. The acid is remarkably unstable, being converted into the coumarin by acids or organic solvents.

The following two ketones obtained from 4:6-dimethylcoumarin correspond in constitution with those prepared from 4:7-dimethylcoumarin (*loc. cit.*). By treatment with alcoholic potassium ethoxide at 160° for twenty-four hours and acidification of the product, 4:6-dimethylcoumarin yields 1-(2:4-*dimethylcoumaran*)-3-(4:6-*dimethyl-*

coumarin) *ketone* (3-[2 : 4-*dimethylhydrocoumarilyl*]-4 : 6-*dimethylcoumarin*), $C_{22}H_{20}O_4$, m. p. 275—280°, which is converted by boiling aqueous-alcoholic alkali into an intensely yellow solution, from which, by acidification, the ketone, $C_{21}H_{22}O_3$, m. p. 199°, already described (*loc. cit.*) is obtained. The ketone, $C_{21}H_{22}O_3$, is converted by ethereal magnesium methyl iodide in the usual way into the *compound*, $C_6H_3Me{<}^{CHMe}_{O}{>}C{:}CMe\cdot CH{<}^{CHMe}_{O}{>}C_6H_3Me$, m. p. 164°, which reacts with bromine in glacial acetic acid to form the *substance*, $C_6H_3Me{<}^{CHMe}_{O}{>}CBr\cdot CMeBr\cdot CBr{<}^{CHMe}_{O}{>}C_6H_3Me$, m. p. 200°. The corresponding compound, $C_{22}H_{24}O_2$, obtained from 4 : 7-dimethylcoumarin (*loc. cit.*), yields by bromination a *substance*, $C_{22}H_{21}O_2Br_5$, m. p. 225°, which has the annexed constitution :



C. S.

Method for the Preparation of Derivatives of α-Cyanoacrylic Acids. C. H. Clarke and Francis Francis (*Ber.*, 1911, 44, 273—276).—Instead of condensing aldehydes with cyanoacetic acid or its ester, the authors use substances which will form cyanoacetic acid, for example, potassium bromoacetate and potassium cyanide :

$$CH_2Br\cdot CO_2K + KCN + R\cdot CHO = R\cdot CH{:}C(CN)\cdot CO_2K + KBr + H_2O.$$

The best yields are obtained when the potassium salt of the bromoacetic acid is added to an aqueous solution of the cyanide and aldehyde. Potassium cyanide accelerates the reaction between aromatic aldehydes and salts of cyanoacetic acid, just as sodium ethoxide does (Carrick, Abstr., 1890, 1270 ; 1892, 1086). The following compounds have been prepared by this method : α-cyanocinnamic acid, α-cyano-β-anisylacrylic acid, α-cyano-β-styrylacrylic acid, α-cyano-β-piperonylacrylic acid, and α-cyano-β-furfurylacrylic acid.

Ethyl α-cyano-β-piperonylacrylate, $C_{13}H_{11}O_4N$, crystallises from alcohol in colourless plates, m. p. 104°. *α-Cyanoferulic acid*,

$$OMe\cdot C_6H_3(OH)\cdot CH{:}C(CN)\cdot CO_2H,$$

prepared from vanillin, potassium bromoacetate, and potassium cyanide, crystallises from dilute alcohol in pale yellow needles, m. p. 215°. The corresponding *ethyl* ester, $C_{13}H_{13}O_4N$, has m. p. 111°.

α-Cyano-o-coumaric acid, $OH\cdot C_6H_4\cdot CH{:}C(CN)\cdot CO_2H$, could not be obtained crystalline ; its *benzoyl* derivative, $C_{17}H_{11}O_4N$, crystallises in needles, m. p. 210°. The acid is hydrolysed with great readiness to coumarinic acid. J. J. S.

Isomeric Phenylphthalimides and Some Allied Compounds. II. Mitsuru Kuhara and Shigeru Komatsu (*Mem. Coll. Sci. Eng. Kyōtō*, 1910, 2, 365—386).—By the action of acetyl chloride on phenylphthalamic acid, the authors (Abstr., 1909, i, 484) have previously obtained two isomeric phenylphthalimides. Of these two isomerides, the colourless form was represented by the formula :

$$C_6H_4{<}^{C(:NPh)}_{CO}{>}O,$$

whilst the yellow variety was supposed to possess a peroxide structure.

The authors now consider that the colour of the yellow isomeride is due to the presence of the chromophoric group C:NPh, and have, therefore, assigned to this form the unsymmetrical formula given above. The constitution of the colourless isomeride remains undetermined.

Two isomeric substituted phenylphthalimides, colourless and yellow, are also produced by the action of phthalyl chloride on *o*-toluidine, *p*-toluidine, *m*-4-xylidine, *o*-3-xylidine, *p*-xylidine, and *ψ*-cumidine. The colourless isomerides possess the symmetrical constitution: $C_6H_4<\substack{CO\\CO}>NAr$, whilst the coloured varieties are represented by the unsymmetrical formula: $C_6H_4<\substack{C(:NAr)\\CO}>O$.

The colourless and yellow modifications of *p*-methoxyphenylphthalimide, *p*-ethoxyphenylphthalimide, and *p*-methoxyphenyl-Δ^1-dihydrophthalimide (Piuti and Abati, Abstr., 1903, i, 424) are considered by the authors to be structural isomerides, the yellow forms having an unsymmetrical, and the colourless varieties a symmetrical structure.

The formulæ assigned by Piutti (Abstr., 1908, i, 783) to the two modifications of *p*-hydroxyphenylmaleimide are to be interchanged.

The behaviour of the isomeric arylphthalimides towards alkylmagnesium halides has also been investigated, and it is found that both isomerides yield the same 3-hydroxy-2-aryl-3-alkyl*iso*indolinone: $C_6H_4<\substack{CO\\CR(OH)}>NAr$ (compare Sachs and Ludwig, Abstr., 1904, i, 266).

It is suggested that the latter compounds are formed from the *as*-arylphthalimides by a molecular arrangement according to the following scheme:

$$C_6H_4<\substack{CO\\C(:NAr)}>O + RMgX + H_2O \longrightarrow \left[C_6H_4<\substack{CR(OH)\\C(:NAr)}>O\right] \longrightarrow$$
$$C_6H_4<\substack{CR(OH)\\CO}>NAr.$$

as-o-*Tolylphthalimide*, $CO<\substack{O\\C_6H_4}>C:N\cdot C_6H_4Me$, obtained together with *s*-*o*-tolylphthalimide by the action of phthalyl chloride on *o*-toluidine in ethereal solution at $-10°$, crystallises in canary-yellow needles, m. p. 136—137°. On treatment with magnesium methyl iodide it yields 3-*hydroxy*-2-o-*tolyl*iso*indolinone*,

$$C_6H_4<\substack{CMe(OH)\\CO}>N\cdot C_6H_4Me;$$

the latter forms colourless crystals, m. p. 161—162°, and is also produced by the action of magnesium methyl iodide on *o*-tolylphthalimide. 3-*Hydroxy*-2-o-*tolyl*-3-*ethyl*iso*indolinone*, $C_{17}H_{17}O_2N$, crystallises in colourless plates, m. p. 169—171°.

as-p-*Tolylphthalimide*, $C_{15}H_{11}O_2N$, crystallises in light yellow needles, m. p. 109—110°, and is formed simultaneously with *s*-*p*-tolylphthalimide by the action of phthalyl chloride on *p*-toluidine; with magnesium ethyl iodide, both these compounds yield 3-*hydroxy*-2-p-*tolyl*-3-

*ethyl*iso*indolinone*, $C_{17}H_{17}O_2N$, which crystallises in colourless needles, m. p. 177—178°.

as-m-4-*Xylylphthalimide*, $CO<\overset{O}{\underset{C_6H_4}{}}>C:N\cdot C_6H_3Me_2$, yellow needles, m. p. 142—143°, m-4-*xylylphthalamide*, $C_6H_4(CO\cdot NH\cdot C_6H_3Me_2)_2$, silky needles, m. p. 202—203°, and s-m-4-*xylylphthalimide*,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot C_6H_3Me_2,$$

slender needles, m. p. 154°, are produced by the interaction of phthalyl chloride and *m*-4-xylidine in ethereal solution. The first-named substance is converted by mineral acids or alkali into *s*-*m*-4-xylyl phthalimide, which is readily obtained by heating *m*-4-xylidine with phthalic anhydride or phthalyl chloride.

Di-m-4-*xylylphthaldi-imide*, $\begin{matrix}C_6H_4\cdot C:N\cdot C_6H_3Me_2\\ | \quad\quad | \\ CO—N\cdot C_6H_3Me_2\end{matrix}$, is produced, together with *s*-*m*-4-xylylphthalimide, by the interaction of phosphorus pentachloride and *m*-4-xylylphthalamide in chloroform solution; it forms yellow plates, m. p. 149—150°.

3-*Hydroxy*-2-m-4-*xylyl*-3-*ethyl*iso*indolinone*,

$$C_6H_4<\begin{matrix}CEt(OH)\\—CO—\end{matrix}>N\cdot C_6H_3Me_2,$$

prepared from both *as*-*m*-4-xylylphthalimide and *s*-*m*-4-xylylphthalimide by the action of magnesium ethyl iodide, crystallises in colourless plates, m. p. 176—177°.

3-*Hydroxy*-2-m-4-*xylyl*-3-*methyl*iso*indolinone*, $C_{17}H_{17}O_2N$, has m. p. 161—162°; from methyl- and ethyl-alcoholic solutions it crystallises with one molecule of alcohol.

o-3-*Xylylphthalamide*, $C_{24}H_{24}O_2N$, slender needles, m. p. 192—193°, is obtained by the interaction of *o*-3-xylidine and phthalyl chloride in ethereal solution; small quantities of a yellow substance, consisting probably of as-o-3-*xylylphthalimide*, $C_{16}H_{13}O_2N$, and of s-o-3-*xylyl phthalimide*, $C_{16}H_{13}O_2N$, are produced simultaneously. The latter compound crystallises in colourless needles, m. p. 143—144°, and is readily obtained by heating *o*-3-xylidine with phthalic anhydride or phthalyl chloride.

Di-o-3-*xylylphthaldi-imide*, $C_{24}H_{22}ON_2$, prepared by the action of phosphorus pentachloride on *o*-3-xylylphthalamide, crystallises from alcohol in yellow plates, m. p. 123—124°.

p-*Xylylphthalamide*, $C_{24}H_{24}O_2N_2$, silky needles, m. p. 209—210°, s-p-*xylylphthalimide*, $C_{16}H_{13}O_2N$, slender needles, m. p. 147—148°, and as-p-*xylylphthalimide*, $C_{16}H_{13}O_2N$, amber-coloured needles, m. p. 178—181°, are obtained by the action of *p*-xylidine on phthalyl chloride in ethereal solution at a low temperature. The last-named substance is unstable, and readily changes into *s*-*p*-xylylphthalimide, which is more easily obtained by heating *p*-xylidine with phthalic anhydride.

Di-p-*xylylphthaldi-imide*, $C_{24}H_{22}ON_2$, obtained from *p*-xylylphthalamide and phosphorus pentachloride, crystallises in yellow plates, m. p. 133—134°.

ψ-Cumylphthalamide, $C_6H_4(CO\cdot NH\cdot C_6H_2Me_3)_2$, silky needles, m. p.

210—212°, and as-*ψ-cumylphthalimide*, $CO<\overset{-O-}{C_6H_4}>C:N\cdot C_6H_2Me_3$, yellow needles, m. p. 117—118°, are obtained together with *s*-*ψ*-cumylphthalimide by the interaction of *ψ*-cumidine and phthalyl chloride.

Di-ψ-cumylphthaldi-imide, $\begin{array}{l}C_6H_4\cdot C:N\cdot C_6H_2Me_3 \\ CO\text{——}N\cdot C_6H_2Me_3\end{array}$, is formed when *ψ*-cumylphthalamide is treated with phosphorus pentachloride in chloroform solution; it crystallises in yellow plates, m. p. 136—137°.

3-Hydroxy-2-ψ-cumyl-3-ethylisoindolinone,

$$C_6H_4<\begin{array}{c}CEt(OH)\\ CO\end{array}>N\cdot C_6H_2Me_3,$$

colourless plates, m. p. 152—153°, is obtained by the action of magnesium ethyl iodide on both forms of *ψ*-cumylphthalimide.

F. B.

Spectrometric Examination of Guthzeit's *cyclo*Butane Derivatives. ERICH HARTMANN (*J. pr. Chem.*, 1911, [ii], 83, 190—194).—The stereoisomerides, $C_{30}H_{44}O_{16}$, m. p. 103° and 88° respectively (Guthzeit, Weiss, and Schäfer, Abstr., 1909, i, 933), and the ester, $C_{30}H_{42}O_{16}$, m. p. 86° (Guthzeit and Hartmann, Abstr., 1910, i, 386), have been examined by the spectrograph. The first two esters give almost identical absorption spectra in alcoholic solution; also in the presence of sodium ethoxide (2 mols.) they give spectra identical, not only with each other, but also with that of ethyl sodiodicarboxyglutaconate; when the three solutions have been acidified, they show the spectrum of ethyl dicarboxyglutaconate. The ester, $C_{30}H_{42}O_{16}$, gives an absorption spectrum which is changed by the addition of sodium ethoxide (2 mols.), but is recovered by acidifying the alkaline alcoholic solution.

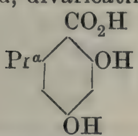
The results, which prove that the first two esters are depolymerised by the addition of sodium ethoxide, whilst the third merely forms a sodium derivative, are in complete harmony with the constitutions ascribed to the three substances (*loc. cit.*). C. S.

Lichens, and their Characteristic Constituents. XII. OSWALD HESSE (*J. pr. Chem.*, 1911, [ii], 83, 22—96).—A scientific classification of the lichens must be based on a chemical examination of their characteristic constituents. The present paper is very largely a repetition of the author's work in this region during the last fifty years. The new work deals mainly with the divergencies of the author's results from those of other observers.

Usnic acid is not a constant constituent of *Evernia prunasti*, as claimed by Zopf (*Flechtenstoffe*, 1907, 356), since the author failed to detect it in several samples of the lichen obtained from different localities. The same statement is true of *Evernia divaricata*.

A large quantity of *E. illyrica*, collected on the Trnovaner Walde, near Görz, has been worked up in the usual way, and the divaricatic acid isolated. It has not the formula $C_{22}H_{26}O_7$, as stated previously, but $C_{21}H_{24}O_7$, which is in agreement with Zopf's analyses. Its decomposition by concentrated hydriodic acid yields methyl iodide, carbon dioxide, and divarinol, not orcinol, as erroneously stated

elsewhere (*Biochemisches Handlexicon*, 7, 69). The *potassium*, *sodium*, *barium*, *calcium*, *copper*, and *silver* salts, the *methyl* and *ethyl* esters, and the *anhydride* are described. The acid, $C_{11}H_{14}O_4$, obtained by the author by boiling divaricatic acid with aqueous barium hydroxide (Abstr., 1898, i, 531), is identical with Zopf's divaricatinic acid, prepared by treating divaricatic acid with potassium hydroxide (Abstr., 1898, i, 489). The *barium* salt, *silver* salt, and *ethyl* ester, m. p. 41°, are described. By treating aqueous sodium divaricatate with an equivalent amount of aqueous ammonia, potassium hydroxide, or sodium hydroxide for forty-eight hours at the ordinary temperature, *divaric acid*, $C_{10}H_{12}O_4$, m. p. 169° (decomp.), is obtained, which in alcoholic solution reddens litmus and develops a purple-violet coloration with ferric chloride. It does not contain a methoxy-group, and is easily decomposed by boiling water, yielding carbon dioxide and divarinol. Pure hydrated divarinol, $C_9H_{12}O_2,H_2O$, has m. p. 44°, and loses its water completely in a desiccator at the ordinary temperature, forming a yellowish-red mass; its *diacetate* has m. p. 12—15°. Divarinol, which resembles orcinol in its behaviour, has the constitution $CPr^a{<}\begin{matrix}CH\cdot C(OH)\\ CH{:}C(OH)\end{matrix}{>}CH$; the annexed formulæ are those of divaric acid, divaricatinic acid, and divaricatic acid respectively: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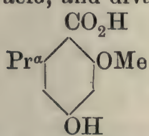
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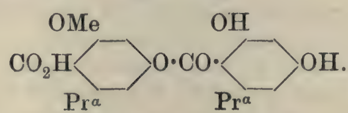


Various samples of *E. furfuracea* have been examined by the author, and found to contain atranorin and evernuric acid, but not farinaceaic acid, as stated by Rave (*Dissert.*, 1908).

Evernia furfuracea, var. *olivetorina* (*Pseudevernia olivetorina*), contains atranorin and olivetoric acid, the *potassium*, *barium*, and *calcium* salts of which are described. The decomposition of olivetoric acid by boiling aqueous barium hydroxide in the absence of air yields carbon dioxide and a substance, *olivetorol*, $C_{20}H_{26}O_5$, which develops a purple-violet coloration with ferric chloride, and a blood-red coloration with calcium hypochlorite; its further examination has been postponed owing to lack of material.

Since Zopf found *l*-usnic acid, destrictic acid, and a colourless crystalline substance in *Cladonia destricta* (Abstr., 1903, i, 762), whilst the author isolated *l*-usnic acid, squamatic acid, cladestin, and some coloured substances (Abstr., 1905, i, 138), the lichen has been again examined, with the result that *l*-usnic acid, cladestin, squamatic acid, destrictic acid, and two new acids, *destrictasic acid* and *cladestic acid*, have been isolated. Destrictasic acid, $C_{15}H_{24}O_2$, m. p. 202°, sintering at 175°, forms white leaflets from dilute alcohol; its alcoholic solution reddens litmus, but does not develop colorations with ferric chloride or calcium hypochlorite.

The following new facts are stated with respect to cladestin: its m. p. is 242—245°, not 252°, it crystallises anhydrous, and it does not yield ethyl iodide by treatment with hydriodic acid, although it is so changed that its alcoholic solution no longer gives a coloration

with ferric chloride. Cladestic acid, $C_{50}H_{74}O_{12}$, is a flesh-coloured, amorphous powder, m. p. 82° (decomp.). It does not contain an alkyloxy-group, has a distinctly acid reaction in alcoholic solution, and develops an intense dark brown coloration with ferric chloride.

Cetraria stuppea contains dilichesteric acid, proto-α-lichesteric acid, and two new substances, called *cornicularin* and *stuppeaic acid*. Cornicularin, $C_{28}H_{44}O_5$, m. p. 230°, is crystalline, does not dissolve in potassium hydroxide or carbonate, and in alcoholic solution gives a dark brown coloration with ferric chloride. Stuppeaic acid, $C_{19}H_{26}O_4$, m. p. 222° (decomp.), is a crystalline powder, dissolves sparingly in the ordinary solvents, gives only a slight brown coloration with ferric chloride, and does not contain an alkyloxy-group. *Cetraria aculeata* contains, in addition to protolichesteric acid and proto-α-lichesteric acid, a new substance called *acanthellin*, $C_{18}H_{34}O_5$, m. p. 188°, which is apparently crystalline, sparingly soluble, and does not give a coloration with ferric chloride.

Stictaic acid, isolated from *Sticta pulmonaria*, probably has the composition $C_{19}H_{14}O_9$, rather than $C_{18}H_{14}O_9$, as stated previously. It is shown that conspersaic acid, isolated from *Parmelia conspersa*, is not identical with salazic acid, as suggested by Zopf (Abstr., 1905, i, 789).

Urceolaria albissima is stated by Zopf (Abstr., 1897, i, 436) to contain zeorin and atranorin, in addition to the lecanoric acid discovered by the author (Abstr., 1899, i, 381), but a repetition of his experiments on 400 grams of the lichen has failed to disclose the presence of these two substances; in one sample, however, atranorin has been discovered. Zopf has stated (Abstr., 1906, i, 672) that the lecanoric acid obtained by the author from *Urceolaria scruposa* (Abstr., 1901, i, 595) is diploschistessic acid; it is now shown that the latter is a mixture of lecanoric and patellaric acids. C. S.

o-Tolylacetaldehyde and its Derivatives. M. KRONIK (*Chem. Zentr.*, 1910, ii, 1051; from *Kosmos*, 1910, **35**, *Radziszewski-Festband*, 590—593).—o-*Tolylacetaldehyde*, $C_6H_4Me\cdot CH_2\cdot CHO$, is obtained by the dry distillation under reduced pressure of the barium salts of *o*-tolylacetic and formic acids; it forms an oily, yellow liquid, b. p. 219—221°/742 mm., b. p. 142—143°/90 mm., D_4^{18} 1·0241, and when diluted has an odour resembling that of jasmine. The *oxime* forms colourless needles, m. p. 99—100°. The *thiosemicarbazone* crystallises in rhombic plates. N. C.

The Carbonyl Group in the Nascent State. ALFRED W. STEWART (*J. pr. Chem.*, 1911, [ii], **83**, 194—197).—Reply to Petrenko-Kritschenko (Abstr., 1910, i, 177). C. S.

Halogenated Alicyclic Ketones. I. Monohalogenides of *cyclo*Hexanones. ARTHUR KÖTZ and H. STEINHORST (*Annalen*, 1911, **379**, 1—27).—The paper deals with the conditions for the direct introduction of one chlorine or bromine atom into *cyclo*hexanone and its homologues, with the orientation of the halogen atom, and with the influence exerted by one or more alkyl groups in the cyclic ketone on

the position of the halogen. It is found that the halogen always enters the ring in the ortho-position to the keto-group, and in the meta- or para-position to a methyl group, when such is present, except in the case of carvomenthone.

The halogenation of the cyclic ketones is effected by Kötz and Götz's process (Abstr., 1908, i, 173), by the action of chlorine, or of bromine vapour mixed with air, in the presence of calcium carbonate and water. The halogenated ketones are deprived of the elements of the hydrogen halogenide by ethereal aniline, and are converted by aqueous potassium carbonate into the corresponding hydroxy-compound, from which the elements of water are removed by anhydrous oxalic acid at 110°; the same *cyclo*hexenone is always obtained by the two processes. Thus *cyclo*hexanone itself has already been shown to yield 2-chloro-(or bromo-)*cyclo*hexanone (Kötz and Götz, *loc. cit.*). 1-Methyl*cyclo*hexan-2-one yields 3-*chloro*-1-*methyl*cyclo*hexan*-2-*one*,

$$CHMe{<}\begin{matrix}CO\cdot CHCl\\ CH_2\cdot CH_2\end{matrix}{>}CH_2,$$

b. p. 98—100°/15 mm., and 3-*bromo*-1-*methyl*cyclo*hexanone*, b. p. 105—107°/12 mm.; the former is converted into 3-*hydroxy*-1-*methyl*-cyclo*hexan*-2-*one*, b. p. 85—87°/13 mm., from which, and also from the bromo-compound, 1-*methyl*-Δ^3-cyclo*hexen*-2-*one*, b. p. 172—173° (*semicarbazone*, m. p. 177—178°), is obtained. 1-Methyl*cyclo*hexan-3-one yields 4-*chloro*-1-*methyl*cyclo*hexan*-2-*one*, m. p. 61—62°, and 4-*bromo*-1-*methyl*cyclo*hexan*-3-*one*, m. p. 83—84°; 4-*hydroxy*-1-*methyl*cyclo*hexan*-3-*one* has b. p. 88—90°/14 mm., and 1-*methyl*-Δ^3-cyclo*hexen*-3-*one*, b. p. 188—190°, forms a *semicarbazone*, m. p. 159—160°. 1-Methyl*cyclo*-hexan-4-one yields 3-*chloro*-1-*methyl*cyclo*hexan*-4-*one*, b. p. 99—101°/14 mm., from which 3-*hydroxy*-1-*methyl*cyclo*hexan*-4-*one*, b. p. 90—92°/14 mm., is obtained; the latter is oxidised to β-methyladipic acid, and yields with anhydrous oxalic acid, 1-*methyl*-Δ^2-cyclo*hexen*-4-*one*, b. p. 175—176° (*semicarbazone*, m. p. 184—185°), which is also obtained from 3-*bromo*-1-*methyl*cyclo*hexan*-4-*one*, b. p. 112—113°/14 mm.

Menthone yields 4-*bromomenthane*-3-*one*, b. p. 120—122°/16 mm., and 4-*chloromenthane*-3-*one*, b. p. 115—117°/15 mm., from which Wallach's Δ^4-menthene-3-one is obtained; an ethereal solution of the last yields with hydrogen chloride, 5-*chloromenthane*-3-*one*, m. p. 135—136°. Carvomenthone yields 1-*chloromenthane*-2-*one*, b. p. 130—132°/14 mm., and 1-*bromomenthane*-2-*one*, b. p. 138—140°/14 mm.; 1-*hydroxymenthane*-2-*one* has b. p. 128—130°/14 mm. The constitutions of the last two compounds are determined by their conversion into carvotanacetone. C. S.

Tetrahydroxybenzenes. GIUSEPPE BARGELLINI and LEDA BINI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 595—600).—The preparation is described of some derivatives of 1 : 2 : 3 : 5-tetrahydroxybenzene including 2 : 3 : 4 : 6-tetramethoxyacetophenone, the corresponding tetramethoxychalkone, and 4 : 2′ : 3′ : 4′ : 6′-pentamethoxychalkone.

When 1 : 2 : 3 : 5-tetramethoxybenzene is treated with acetyl chloride in presence of aluminium chloride in carbon disulphide solution, a mixture of the dimethyl (in small quantity), trimethyl, and tetramethyl ethers of 2:3:4:6-tetrahydroxyacetophenone is produced. The

first two are soluble in sodium hydroxide; they can be precipitated from it by addition of acid, and separated with the aid of solvents. 2:3:4:6-*Tetrahydroxyacetophenone dimethyl ether*, $C_{10}H_{12}O_5$, is a bright yellow, crystalline powder, m. p. 162—163°. It dissolves in concentrated sulphuric acid with production of an orange-yellow coloration, which on addition of nitric acid becomes intensely red. Its *acetyl* derivative has m. p. 110—112°. 2:3:4:6-*Tetrahydroxyacetophenone trimethyl ether*, $C_{11}H_{14}O_5$, forms slightly yellow, prismatic crystals, m. p. 105—107°, and dissolves in concentrated sulphuric acid, giving a yellow coloration which becomes red on addition of nitric acid. Its *acetyl* derivative, $C_{13}H_{16}O_6$, crystallises in small, colourless needles, m. p. 106°. The *benzoyl* derivative has m. p. 120—122°. 2:3:4:6-*Tetrahydroxyacetophenone tetramethyl ether*, $C_{12}H_{16}O_5$, has m. p. 43—45°, b. p. about 310°, and gives a yellow solution in concentrated sulphuric acid, which becomes intensely red when treated with nitric acid. Its *semicarbazone*, $C_{13}H_{19}O_5N_3$, forms small, colourless needles, m. p. 128—130°. 2′:3′:4′:6′-*Tetramethoxychalkone* (from benzaldehyde) crystallises in tufts of small, very pale yellow needles, m. p. 74—75° (softening at 70°). It dissolves in concentrated sulphuric acid with production of an orange-red coloration. 4:2′:3′:4′:6′-*Pentamethoxychalkone*, $C_{20}H_{22}O_6$ (from anisaldehyde), forms small, straw-yellow needles, m. p. 88—90° (previously softening), and dissolves in concentrated sulphuric acid with production of an orange-red coloration.

R. V. S.

α-Amino-ketones. SIEGMUND GABRIEL (*Ber.*, 1911, 44, 57—69).—A description is given of the preparation of some α-amino-ketones of the type $X\cdot CO\cdot CR_2\cdot NH_2$, hitherto unknown. *α-Phthaliminoiso-butyric acid*, $C_6H_4<{CO \atop CO}>N\cdot CMe_2\cdot CO_2H$, m. p. 153—154°, obtained from α-amino*iso*butyric acid and phthalic anhydride at 180°, is converted by phosphorus pentachloride into the *chloride*,

$$C_6H_4<{CO \atop CO}>N\cdot CMe_2\cdot COCl,$$

m. p. 82—84°. By treatment with benzene and aluminium chloride, and subsequently with cold dilute hydrochloric acid, the chloride is converted into *α-phthaliminoisobutyrophenone*, m. p. 122—123·5°, which on hydrolysis by hot 10% potassium hydroxide and subsequent treatment with hydrochloric acid yields *α-aminoisobutyrophenone hydrochloride*, $COPh\cdot CMe_2\cdot NH_2,HCl,\frac{1}{2}H_2O$, sintering at about 137°; the anhydrous salt has m. p. 187—188°; the *picrate*, m. p. 175°. Unlike other α-amino-ketones, the salt of this new amino-ketone does not reduce Fehling's solution. *α-Aminoisobutyrophenone*, liberated from the hydrochloride by strong potassium hydroxide, has b. p. 254—255°/752 mm., and is the first α-amino-ketone that has been isolated in the pure state, others suffering condensation and oxidation to substituted pyrazines (Abstr., 1908, i, 464).

A suspension of ethyl sodiomalonate in benzene is treated with a benzene solution of α-phthalimino*iso*butyryl chloride, and the yellow solution obtained is boiled for eighteen hours, neutralised by a little hydrochloric acid, and distilled with steam; the yellow residue is extracted

with ether (the insoluble yellow, crystalline powder is described in the following abstract), the ethereal filtrate, after being shaken with aqueous sodium carbonate, is evaporated, and the residue is dissolved in lukewarm amyl alcohol, the solution being kept for six hours at the ordinary temperature, whereby *ethyl a-phthaliminoisobutyrylmalonate*, $C_6H_4<\substack{CO\\CO}>N\cdot CMe_2\cdot CO\cdot CH(CO_2Et)_2$, m. p. 76—77·5°, is obtained. When boiled with hydriodic acid, b. p. 127°, for half an hour, the ester is decomposed into phthalic acid, carbon dioxide, ethyl iodide, and *methyl β-aminoisopropyl ketone hydriodide*,

$$CH_3\cdot CO\cdot CMe_2\cdot NH_2,HI,$$

m. p. 169—170°. The *nitrate*, m. p. 132—133·5°, *hydrochloride*, m. p. 210—211°, *platinichloride*, m. p. 201° (decomp.), *aurichloride*, m. p. 165°, giving turbid liquid clarifying at 190°, *picrate*, m. p. 142—143·5°, *benzoyl* derivative, m. p. 124—125°, and *phthalyl* compound,

$$C_6H_4<\substack{CO\\CO}>N\cdot CMe_2\cdot COMe,$$

m. p. 105—106°, are described. The aqueous solutions of the salts of this α-amino-ketone do not reduce Fehling's solution. Unlike α-amino-*iso*butyrophenone, however, this amino-ketone cannot be isolated in a pure state. When an aqueous solution of its hydriodide is treated with an equivalent amount of *N*-sodium hydroxide, a certain amount of the amino-ketone is obtained together with a crystalline substance with an odour of menthol. The latter is obtained better by shaking the solid hydriodide with an excess of 33% potassium hydroxide; it has m. p. 88—89°, and is the hexahydrate of a *base*, $C_{10}H_{18}N_2$, b. p. 180—881°, m. p. 69—69·5°, which volatilises very readily and appears to be 2 : 3 : 3 : 5 : 6 : 6-*hexamethyl*-3 : 6-*dihydropyrazine*,

$$N\leqslant\substack{CMe\cdot CMe_2\\CMe_2\cdot CMe}\geqslant N;$$

its *hydrochloride*, *picrate*, m. p. 232° (decomp.), *platinichloride*, and *aurichloride*, decomp. 180°, are described. By reducing the base with sodium and alcohol, and treating the product with hydrochloric acid and potassium nitrite, *dinitrosohexamethylpiperazine*, $C_{10}H_{20}O_2N_4$, m. p. 248—249° (decomp.), is obtained, which is converted by boiling hydrochloric and a little acetic acids into *hexamethylpiperazine hydrochloride*, $C_{10}H_{22}N_2,2HCl$, from which the hydrated *base*, $C_{10}H_{22}N_2,2H_2O$, m. p. 65—66·5°, is obtained by the action of concentrated potassium hydroxide; the *nitrate*, *platinichloride*, *aurichloride*, *picrate*, decomp. 260°, and *mercurichloride* are mentioned. A by-product of the action of very concentrated potassium hydroxide on methyl β-amino*iso*propyl ketone hydriodide is a basic *substance*, $C_{10}H_{18}N_2$, which forms a *hydrochloride*, $C_{10}H_{18}N_2,2HCl,2H_2O$, m. p. about 171—172°, *platinichloride*, $C_{10}H_{18}N_2,H_2PtCl_6$, *benzoyl* derivative, $C_{10}H_{17}N_2Bz$, m. p. 105°, *picrate*, m. p. 198°, and *aurichloride*. Its constitution has not yet been ascertained; probably it is an aminopyrrole or pyridine derivative.

C. S.

The Beckmann Rearrangement. II. MITSURU KUHARA and YOSHINORI TODO (*Mem. Coll. Sci. Eng. Kyōto*, 1910, 2, 387—396).—The influence of acetyl chloride, chloroacetyl chloride, and benzene-

sulphonyl chloride on the rate of rearrangement of diphenylketoxime has been determined by heating a chloroform solution of the acid chloride and the oxime in molecular proportions at 60°, and weighing the benzanilide produced.

In $\frac{1}{2}$-molar solutions, diphenylketoxime is almost completely transformed into benzanilide by benzenesulphonyl chloride in five minutes, whilst with chloroacetyl chloride, 61% undergoes change in the same time; in the case of acetyl chloride the rate of rearrangement is much slower, only 9·4% of the oxime being transformed in fifteen minutes.

The rates of rearrangement thus stand in the order of magnitude of the dissociation constants of the acids, and the conclusion is therefore drawn that the velocity of transformation of the oxime esters, $CPh_2\colon N\cdot O\cdot CO\cdot R$, is dependent on the negative character of the acid residue $R\cdot CO\cdot O$.

Measurements of the velocity of rearrangement of acetyldiphenylketoxime in the presence of hydrochloric acid, and of diphenylketoxime in the presence of acetyl chloride, both in $\frac{1}{2}$-molar chloroform solutions, indicate that these reactions are unimolecular.

With respect to the mechanism of the rearrangement, the authors propose the following scheme:

$$\begin{array}{c}\mathrm{Ph\,C\,Ph}\\ \|\\ \mathrm{N\cdot OH}\end{array} + \mathrm{AcCl} \xrightarrow{(1)} \begin{array}{c}\mathrm{Ph\,C\,Ph}\\ \|\\ \mathrm{HClN\cdot OAc}\end{array} \xrightarrow{(2)} \begin{array}{c}\mathrm{PhC\cdot OAc}\\ \|\\ \mathrm{HClNPh}\end{array} \xrightarrow{(3)} \begin{array}{c}\mathrm{PhCO}\\ |\\ \mathrm{HNPh}\end{array} + \mathrm{AcCl},$$

in which the changes (1) and (3) take place rapidly, whilst the reaction (2) occurs slowly, thus accounting for the transformation being, apparently, of the unimolecular type.

According to the authors, the primary cause of the change:

$$(\mathrm{I})\ \begin{array}{c}\mathrm{R\cdot C\cdot R}\\ \|\\ \mathrm{N\cdot O\cdot COR'}\end{array} \longrightarrow (\mathrm{II})\ \begin{array}{c}\mathrm{R\cdot C\cdot O\cdot COR'}\\ \|\\ \mathrm{N\cdot R}\end{array}$$

is the negative character of the acid residue $R'CO\cdot O$; with strongly negative residues, dissociation of (I) into $R_2C\colon N^-$ and $R'CO\cdot O$ readily takes place, and these dissociation products then react to form (II).

It has been shown (Kuhara and Kainosho, Abstr., 1907, i, 1027) that the presence of hydrochloric acid is necessary for the rearrangement of acetyldiphenylketoxime, and the authors therefore draw the conclusion that in the case of the oxime-acetates, hydrochlorides of the type $CR_2\colon N\cdot OAc,HCl$ are produced; under the influence of the hydrochloric acid, the tendency of the OAc group to separate from the nitrogen atom is increased to such an extent that a similar dissociation to that mentioned above takes place.

A *compound* of the constitution $OAc\cdot CPh\colon NPh$ has been obtained as a viscid, yellow oil by the interaction of the imide-chloride, $CPhCl\colon NPh$, and silver acetate. On passing hydrochloric acid into its cold ethereal solution, the *hydrochloride* separates out as a canary-yellow precipitate, which is converted by excess of the acid into acetylbenzanilide. When the hydrochloride in chloroform solution is heated above 60°, it yields benzanilide. This change corresponds with the last phase of the rearrangement in the authors scheme given above.
F. B.

Ketens. XV. Action of Diphenylketen on Nitroso-compounds. HERMANN STAUDINGER and SERGIUS JELAGIN (*Ber.*, 1911, 44, 365—374. Compare Abstr., 1910, i, 46).—By the action of nitrosodimethylaniline in ethereal solution in 2 mols. of diphenylketen, carbon dioxide is liberated, the green colour at once vanishes, and the Schiff's base first formed combines with diphenylketen to form a *β-lactam* of *β-dimethylaminoanilino-ααββ-tetraphenylpropionic acid*, $CPh_2<\substack{-CO-\\ CPh_2}>N\cdot C_6H_4\cdot NMe_2$. This forms colourless crystals, which sinter at 196°, m. p. above 200° (decomp. to an orange-red liquid). The composition of this lactam was proved by its synthesis from diphenylketen and benzophenone-*p*-dimethylaminoanil.

Nitrosobenzene reacts differently with diphenylketen, forming *anhydrodiphenylglycollylphenylhydroxylamine*, $CPh_2<\substack{CO\\ O}>NPh$, which separates in well formed, colourless crystals, m. p. 72·5°. It is stable at the melting point, but, on further heating, decomposes explosively into benzophenone and phenylcarbimide. When boiled with concentrated hydrochloric acid, *chlorodiphenylacetophenylhydroxylamine*, $CPh_2Cl\cdot CO\cdot NPh\cdot OH$, colourless crystals, m. p. 158·5—159·5°, is formed. The four-membered ring-compound is obtained synthetically by the action of chlorodiphenylacetyl chloride on phenylhydroxylamine.

Nitrosobenzene and 2 mols. of diphenylketen also react to form small quantities of the *β-lactam* of *β-anilino-ααββ-tetraphenylpropionic acid*, $CPh_2<\substack{-CO-\\ CPh_2}>NPh$, m. p. 191°, which is also formed on condensing benzophenoneanil with diphenylketen. The four-membered ring, $CPh_2<\substack{-CO-\\ NPh}>O$, is possibly formed in small quantity during the action of nitrosobenzene on diphenylketen, but decomposes in the cold into benzophenoneanil and carbon dioxide.

Diphenyl- and dimethyl-nitrosoamines do not react with diphenylketen. E. F. A.

Action of Nitric Acid on Halogen Derivatives of *o*-Alkylated Phenols. II. THEODOR ZINCKE and W. BREITWEISER (*Ber.*, 1911, 44, 176—184).—The products formed by the action of nitric acid on tribromo-*p*-xylenol are similar to those obtained previously from tetrabromo-*o*-cresol (Abstr., 1907, i, 322). They are three in number, namely: (*a*) 3 : 5 : 6-tribromo-1 : 4-dimethylquinonitrole,

$$CMe<\substack{CBr-CO\\ CBr:CBr}>CMe\cdot NO_2.$$

(*b*) An additive compound of the quinonitrole with nitric acid,

$$CMe<\substack{CBr\cdot C(OH)(O\cdot NO_2)\\ CBr=\!=\!=\!=\!=\!=CBr}>CMe\cdot NO_2.$$

(*c*) An open-chain compound, $NO_2\cdot CHMe\cdot CBr:CBr\cdot CMe:CBr\cdot CO\cdot ONO_2$, which can also be obtained by the action of sodium carbonate solution on the additive compound.

The quinonitrole is identical with the product described by Auwers (Abstr., 1899, i, 30), but is regarded as an ortho- and not a para-

derivative, since the quinole obtained by the action of cold benzene on the nitro-compound does not lose hydrogen bromide and form dibromo-*p*-xyloquinone, and does not yield a *p*-xyloquinone derivative when heated with sodium acetate and acetic anhydride, but loses nitrous acid extremely readily under the influence of moist ether, yielding 3 : 5 : 6-tribromo-4-methyl-*o*-methylenequinone,

$$CMe\lessdot\begin{matrix}CBr\colon CBr\\CBr\cdot CO-\end{matrix}\!\!>C\colon CH_2.$$

The conversion of the quinonitrole into dibromo-*p*-xyloquinone by boiling with benzene or light petroleum, and of the quinole into dibromo-*p*-xyloquinone by warming with acetic anhydride and concentrated sulphuric acid is accompanied by molecular rearrangements.

3 : 4 : 6-Tribromo-1 : 4-dimethylquinonitrole is most readily prepared by the action of concentrated nitric acid on tribromo-*p*-xylenol in the presence of glacial acetic acid. It reacts with cold methyl alcohol, yielding 3 : 6 - *dibromo*-5 - *nitro* - p - 2 - *xylenol*, $NO_2\cdot C_6Me_2Br_2\cdot OH$, as colourless needles, m. p. 154°, together with a product, m. p. 186—190°, insoluble in alkalis, and with acetic anhydride and a few drops of concentrated sulphuric acid yields *dibromo*-p-*xyloquinol diacetate* in the form of yellowish-white needles, m. p. 218°. 3 : 5 : 6-*Tribromo*-1 : 4-*dimethylquinol*, $C_8H_7O_2Br_3$, crystallises from light petroleum in colourless needles, m. p. 111°.

3 : 5 : 6 - *Tribromo*-4-*methyl*-o-*methylenequinone*, $C_8H_5OBr_3$, crystallises from acetic anhydride in yellow plates, m. p. 220—230° (decomp.), and is not chemically active. The *acetyl* derivative of 3 : 6-dibromo-5-nitro-*p*-2-xylenol crystallises in colourless, glistening prisms, m. p. 116°, and 3 : 6-*dibromo*-4-*amino*-p-2-*xylenol* crystallises from benzene in colourless plates, m. p. 186—188°. The additive *compound* of the quinonitrole with nitric acid, $C_8H_7O_6N_2Br_3$, crystallises in colourless, well-developed prisms, m. p. 105—107° (decomp.). The open-chain *compound*, $C_8H_7O_6N_2Br_3$, crystallises in colourless needles, m. p. 141° (decomp.). J. J. S.

Oxidation of Aniline. II. RIKŌ MAJIMA (*Ber.*, 1911, 44, 229—234. Compare Willstätter and Majima, Abstr., 1910, i, 748).—By the oxidation of aniline with sodium bromate in aqueous acetic acid solution at 0°, a mixture of 2 : 5-dianilino-*p*-benzoquinoneanil and *amino-anilino*-p-*benzoquinoneanil*,

$$O\colon C<\begin{matrix}CH{=}{=}C(NH_2)\\C(NHPh)\colon CH\end{matrix}>C\colon NPh \text{ or } O\colon C<\begin{matrix}C(NH_2){=}{=}CH\\CH\colon C(NHPh)\end{matrix}>C\colon NPh,$$

is produced. The latter compound, isolated by means of its sparingly soluble *sulphate*, crystallises in bluish-red prisms. It dissolves in concentrated sulphuric acid with a green colour, has feebly basic properties, and yields 2 : 5-dianilino-*p*-benzoquinoneanil when heated with aniline in glacial acetic acid solution. The *hydrochloride*, $C_{18}H_{15}ON_3,HCl$, forms dark green crystals.

2 : 5-Dianilino-*p*-benzoquinoneimine (Willstätter and Majima, *loc. cit.*) is more conveniently prepared by oxidising aniline with sodium persulphate. When hydrolysed with hydrochloric acid in aqueous alcoholic solution, it yields 2 : 5-dianilino-*p*-benzoquinone. F. B.

Synthesis of β-Menthol-lactoside and its Behaviour in the Organism. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1911, 70, 256—263. Compare E. and H. Fischer, Abstr., 1910, i, 716).—*Hepta-acetyl-β-menthol-lactoside*, prepared by the interaction of acetobromolactose and menthol in presence of silver carbonate and chloroform, crystallises in long prisms, m. p. 125—130°, $[\alpha]_D^{19}$ $-29\cdot65°(\pm 0\cdot2)$. It resists hydrolysis by dilute mineral acids; barium hydroxide converts it into *β-menthol-lactoside*. This crystallises with $4H_2O$ in concentrically-grouped prismatic needles, m. p. 110°, $[\alpha]_D^{16}$ $-38\cdot04°$. It is hydrolysed by mineral acids to menthol and reducing sugar, and by emulsin to menthol, lactose, and some dextrose. Kephir lactose hydrolyses it slowly.

When injected subcutaneously into the organism, it is excreted unchanged; neither mentholglycuronic acid nor menthol-lacturonic acid are formed.

Mentholglycuronic acid ($1\frac{1}{2}H_2O$) sinters at 92°, m. p. 110°, and has $[\alpha]_D^{20}$ $-104\cdot4°$. E. F. A.

Some Derivatives of Dicamphor. VINCENZO CASTELLANA and R. FERRERO (*Gazzetta*, 1910, 40, ii, 482—491. Compare Angeli, Castellana, and Ferrero, Abstr., 1909, i, 739).—When pernitrosodicamphor is boiled with an excess of alcoholic potassium hydroxide, the *potassium* salt separates as a precipitate. If water is added to dissolve this, the boiling continued for an hour, and then the alcohol removed by distillation, *dicamphenoneimine* remains as an oil, which on cooling solidifies and after recrystallisation forms needles, m. p. 191°. If the ebullition is prolonged for several hours, an amorphous, grey powder having the properties of an *acid* is obtained on acidifying the wash water of the preceding compound. To the imine the structure $C_8H_{14}<\begin{matrix}C\!=\!=\!=\!=\!=C\\ |\qquad\quad |\\ C{:}NH\quad OC\end{matrix}>C_8H_{14}$ is ascribed. It forms a *picrate*, $C_{20}H_{29}ON,C_6H_2(NO_2)_3OH$, m. p. 195°. When warmed with dilute sulphuric acid, the imine yields the corresponding diketone, *dicamphenone*, $C_8H_{14}<\begin{matrix}C\!=\!=\!=C\\ |\qquad |\\ CO\quad OC\end{matrix}>C_8H_{14}$, which crystallises in lemon-yellow needles, m. p. 192—193°, and is identical with the dicamphanehexanedione of Oddo (Abstr., 1897, i, 577). With hydrazine, it yields the azine, as stated by that author, and at the same time a small quantity of a yellow *substance*, m. p. 153°, is formed. The same azine is obtained from hydrazine and pernitrosodicamphor. Its *picrate*, $C_{20}H_{28}N_2,C_6H_3O_7N_3$, has m. p. 220°.

Pernitrosodicamphor when treated with an excess of hydroxylamine yields two products which can be separated with the aid of solvents, and are apparently stereoisomeric *dioximes*, $C_{20}H_{32}O_2N_2$. One is crystalline, and has m. p. about 240° (decomp.); the other is formed in very small amount, and has m. p. about 275—280°.

The authors have also prepared pernitrosocamphor and some of its derivatives from inactive camphor, and find them to have similar properties, but somewhat lower melting points: *pernitroso*-i-*camphor* has m. p. 32°; *pernitrosodi*-i-*camphor*, m. p. 163°; i-*dicamphenoneimine*, m. p. 179°. R. V. S.

Behaviour of Iodine towards Terpine Hydrate, Eucalyptol, and Terpineol. CARLO CASANOVA (*Boll. chim. farm.*, 1910, 49, 957—960. Compare Abstr., 1909, i, 813).—The above terpenes react with iodine on warming, and the liquid compounds produced are heavier than water and give no reaction with starch. They readily decompose in the course of a few hours if exposed to light and air, large quantities of iodine and hydrogen iodide being set free.

R. V. S.

Constituents of Ethereal Oils. Constitution of Perillaldehyde, $C_{10}H_{14}O$. FRIEDRICH W. SEMMLER and B. ZAAR (*Ber.*, 1911, 44, 52—57).—The aldehyde isolated from *Perilla nankinensis* leaf oil, and described by Schimmel & Co. (Abstr., 1910, i, 758), has been isolated and examined by the authors. In addition to the properties already recorded (*loc. cit.*), the aldehyde, which is called perillaldehyde, shows the following behaviour. The *semicarbazone* has m. p. 199—200°. By reduction with zinc dust and glacial acetic acid on the water-bath, the aldehyde yields perillyl alcohol in the form of its *acetate*, $C_{12}H_{18}O_2$, b. p. 123—126°/13 mm., D^{20} 0·9785, n_D 1·48142, $[\alpha]_D$ −48°; the *alcohol*, $C_{10}H_{16}O$, obtained by hydrolysing the ester by alcoholic potassium hydroxide, has b. p. 119—121°/11 mm., D^{20} 0·9640, n_D 1·49964, $[\alpha]_D$ −68·5°, and is converted by phosphorus pentachloride in petroleum solution into the *chloride*, $C_{10}H_{15}Cl$, b. p. 99—101°/12 mm., D^{20} 0·9861, n_D 1·49728, $[\alpha]_D$ −60°. By treatment with sodium and alcohol, the chloride is converted into *l*-limonene.

Perillaldoxime is changed by boiling acetic anhydride and sodium acetate into *perillonitrile*, $C_{10}H_{13}N$, b. p. 116—118°/11 mm., D^{20} 0·9439, n_D 1·49775, $[\alpha]_D$ −115°, which by hydrolysis yields *perillic acid*, $C_{10}H_{14}O_2$, b. p. 164—165°/10 mm., m. p. 130—131°, $[\alpha]_D$ −20° in 25% alcoholic solution. The acid forms a *dibromide*, $C_{10}H_{14}O_2Br_2$, m. p. 166—167°, and is reduced by sodium and boiling amyl alcohol to *dihydroperillic acid*, $C_{10}H_{16}O_2$, b. p. 152—153°/10·5 mm., m. p. 107—109°, $[\alpha]_D$ 0° in 25% alcoholic solution, which forms a *dibromide*, m. p. 116—117°, and a *methyl* ester (from the silver salt and methyl iodide), b. p. 105—106°/11 mm., D^{18} 0·9732, n_D 1·46768, $[\alpha]_D$ 0°, from which *dihydroperillyl alcohol*, $C_{10}H_{18}O$, b. p. 114—115°/10 mm., D^{19} 0·9284, n_D 1·48191, $[\alpha]_D$ 0°, is obtained by the action of sodium in the usual way.

The formation of the preceding derivatives, particularly of *l*-limonene, and the fact that the molecular refraction of perillaldehyde indicates the presence of two ethylenic lingings, afford good evidence of the constitution $CH_2{:}CMe{\cdot}CH{<}{\begin{smallmatrix}CH_2\cdot CH_2\\ CH_2-CH\end{smallmatrix}}{\gg}C{\cdot}CHO$ for the aldehyde.

C. S.

Curcumin. C. LORING JACKSON and LATHAM CLARKE (*Amer. Chem. J.*, 1911, 45, 48—58).—Miłobędzka, Kostanecki, and Lampe's statement (Abstr., 1910, i, 629) that curcumin should be represented by the formula $C_{21}H_{20}O_6$, first proposed by Ciamician and Silber (Abstr., 1897, i, 229), instead of $C_{14}H_{14}O_4$, as suggested by Jackson and Menke (*Amer. Chem. J.*, 1884, 4, 77), is confirmed. Curcumin has m. p. 178°,

as found by Jackson and Menke, and not 183°, as stated by Ciamician and Silber. Curcumin dimethyl ether has m. p. 137°, instead of 135°, as recorded by Ciamician and Silber, and can be obtained in a quantitative yield by using a shaking machine instead of applying heat.

The brown coloration produced by the action of hydrogen chloride on curcumin is due to the formation of an additive *compound*, which is dark brown when only a little hydrogen chloride is used, but becomes dark violet when an excess is employed; it is very unstable, and is instantly decomposed by water. A similar *compound*,

$$C_{21}H_{20}O_6,3HBr,$$

is formed by the action of hydrogen bromide. The reddish-purple substance formed by the action of phosphoryl chloride on curcumin (Jackson and Menke, *loc. cit.*) is probably either the hydrogen chloride additive compound or a similar product containing chlorine and phosphorus, since it is reconverted into curcumin by the action of water. This substance, if left in a desiccator, becomes black, owing to the further action of the phosphoryl chloride.

When an alcoholic solution of curcumin is shaken for a long time with hydroxylamine hydrochloride, a *compound*, m. p. 162°, probably the mono-oxime, is produced, which forms stout, orange-yellow needles. If the mixture is heated on the steam-bath instead of being shaken at the ordinary temperature, a yellowish-white compound, m. p. 163°, is obtained, which is probably identical with the foregoing, although of a different colour. This substance is not identical with the *iso*oxazole described by Ciamician and Silber (*loc. cit.*). E. G.

Pyronone Synthesis by means of the "Tertiary Bases Reaction." II. EDGAR WEDEKIND [and JOHANNES HÄUSSERMANN, W. WEISSWANGE, and MORIZ MILLER] (*Annalen*, 1911, **378**, 261—292).—The "tertiary bases reaction" (Wedekind and Häussermann, Abstr., 1908, i, 671) has been applied to phenylacetyl chloride, phenylpropionyl chloride, *p*-nitrophenylacetyl chloride, and butyryl chloride; pyronone derivatives are formed, the production of a diketo-*cyclo*butane, as in the case of *iso*butyryl chloride (Wedekind and Weisswange, Abstr., 1906, i, 437), not being observed.

Thus by slowly adding a solution of phenylacetyl chloride (1 mol.) in dry carbon disulphide to a solution of a tertiary base (tripropylamine, pyridine, 1-methylpiperidine, or, best of all, triethylamine) in the same solvent at 0°, moisture being rigorously excluded by passing a slow stream of dry hydrogen through the apparatus, 3 : 5-*diphenyl*-2-*benzyl*-1 : 4 : 6-*pyronone*, $CO{<}\begin{matrix}CHPh\text{——}CO\\CPh{:}C(CH_2Ph)\end{matrix}{>}O$, m. p. 173—174°, is obtained in 50% yield, its formation being explained in the same way as that of 3 : 5-dimethyl-2-ethyl-1 : 4 : 6-pyronone from propionyl chloride (Wedekind and Häussermann, *loc. cit.*). The substance is remarkably stable to reducing agents, behaves as a monobasic acid (*sodium* salt, $C_{24}H_{17}O_3Na,3EtOH$, colourless crystals from alcohol), but not as an oxonium base, and is decomposed by 20% potassium hydroxide into diphenylacetone, phenylacetic acid, and carbon dioxide. This reaction suggests that the substance might be *s*-triphenylphloro-

glucinol, produced by the polymerisation of 3 mols. of phenylketen. Its pyronone constitution, however, is indicated by the formation of a *mono-oxime*, m. p. 157° (decomp.), *acetate*, $C_{26}H_{20}O_4$, m. p. 124—125°, and *benzoate*, $C_{31}H_{22}O_4$, m. p. 126°, by the non-formation of triphenylbenzene by reduction with zinc dust, and by its behaviour with concentrated aqueous ammonia at 80—100° and finally at 130—140°, whereby 4 : 6-*dihydroxy*-3 : 5-*diphenyl*-2-*benzylpyridine*,

$$N{<}{\substack{C(CH_2Ph){:}CPh \\ C(OH){=\!=}CPh}}{>}C{\cdot}OH,$$

m. p. 260°, is obtained. This substance has acidic properties, does not decolorise bromine, develops a reddish-brown coloration with alcoholic ferric chloride (distinction from the pyronone), and forms a *diacetate*, m. p. 165°. The ready formation of an oxime from diphenylbenzylpyronone is unusual; its oximic structure is proved by the regeneration of hydroxylamine and the pyronone by hydrolysis with concentrated hydrochloric acid.

Phenylpropionyl chloride and tripropylamine, reacting under the preceding conditions, yield 3: 5-*dibenzyl*-2-β-*phenylethyl*-1 : 4 : 6-*pyronone*, $CH_2Ph{\cdot}CH_2{\cdot}C{<}{\substack{C(CH_2Ph){\cdot}CO \\ O{-\!-\!-\!-}CO}}{>}CH{\cdot}CH_2Ph$, m. p. 167—168°, which resembles diphenylbenzylpyronone, but is less acidic, does not form an oxime, and is more readily decomposed by 25% potassium hydroxide at 120°, yielding dibenzylacetone, phenylpropionic acid, and carbon dioxide.

Butyryl chloride and triethylamine react in carbon disulphide to form a pyronone derivative, which is so unstable, however, that its production is indicated only by the formation of dipropyl ketone resulting from its decomposition.

p-*Nitrophenylacetyl chloride*, b. p. 135—138°/0·1 mm., m. p. 47°, obtained from the acid and phosphorus pentachloride, reacts with triethylamine in dry ether cooled by a freezing mixture, 3 : 5-*di*-p-*nitrophenyl*-2-p-*nitrobenzyl*-1 : 4 : 6-*pyronone*,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}C{<}{\substack{C(C_6H_4{\cdot}NO_2){\cdot}CO \\ O{-\!-\!-\!-\!-\!-}CO}}{>}CH{\cdot}C_6H_4{\cdot}NO_2,$$

m. p. 146° (decomp.), a yellow, microcrystalline powder, being produced, which has pronounced acidic properties and is decomposed by 20% potassium hydroxide at 160°, yielding *p*-nitrophenylacetic acid and pp′-*dinitrodiphenylacetone*, decomp. 205—206° (*phenylhydrazone*, decomp. 110—112°).

The "tertiary bases reaction" has also been applied to *iso*valeryl chloride and crotonyl chloride; the former with ethereal tripropylamine yields ethyl *iso*valerate and *iso*valeric anhydride, whilst the latter with triethylamine in benzene forms crotonic anhydride.

C. S.

"Oxindigo" [2:2′-Diketo-$\Delta^{1:1'}$-dicoumaran]. RICHARD STOERMER and K. BRACHMANN (*Ber.*, 1911, **44**, 315—319).—The yellow substance, m. p. 276° (decomp.), obtained by acidifying the potassium salt of *aci*-nitrocoumaranone and formerly regarded as "leuco-oxindigo" (Abstr., 1909, i, 174), is now found to be 2 : 2′-diketo-$\Delta^{1:1'}$-dicoumaran itself, since it is produced from the potassium salt by the action of iodine in

aqueous potassium iodide or alcohol, a reaction in which the formation of "leuco-oxindigo" [2 : 2′-dihydroxy-1 : 1′-dicoumaran] is impossible. The properties of the substance correspond almost exactly with those of 2 : 2′-diketo-$\Delta^{1:1'}$-dicoumaran prepared by Fries and Hasselbach (this vol., i, 150).

The action of chlorine water on potassium *aci*-nitrocoumaranone yields 1-*chloro*-1-*nitrocoumaranone*, $C_8H_4O_4NCl$, m. p. 102°. 1-*Bromo*-1-*nitrocoumaranone*, m. p. 105°, is obtained by shaking the potassium salt with bromine in benzene, or by rapidly adding bromine water to its aqueous solution; when the bromine water is added very slowly, diketo-$\Delta^{1:1'}$-dicoumaran is produced. C. S.

Coffee. IV. K. Gorter (*Annalen*, 1911, **379**, 110—130. Compare Abstr., 1908, i, 186, 345).—The author replies to Lendrich and Nottbohm's criticism (Abstr., 1909, ii, 449) of his method for the estimation of the caffeine in raw coffee (*loc. cit.*), and describes experiments which show that the caffeine in Liberian coffee is all present as potassium caffeine chlorogenate.

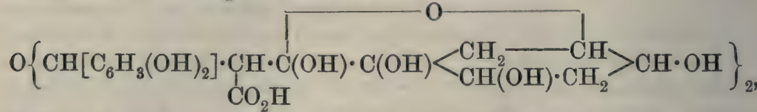
All formulæ previously suggested for hemichlorogenic acid are withdrawn and are replaced by the constitution given below for the following reasons: (1) In its fission by acids and alkalis, hemichlorogenic acid behaves like a β-ketonic acid. (2) The non-formation of an oxime, phenylhydrazone, and semicarbazone indicates the absence of a carbonyl group. (3) If the tetrahydropyrone formula previously suggested is correct, the acid should yield 3′ : 4′-dihydroxyflavone by the elimination of $3H_2O$ and of the carboxyl group. This result has not been effected by heating chlorogenic acid with hydriodic acid, with water at 220—230°, or alone at 240—250° in a vacuum. (4) By treatment with bromine (1 mol.) in chloroform in sunlight, penta-acetylhemichlorogenic acid yields a crystalline, additive *compound*, $C_{16}H_{13}O_9Ac_5Br_2$, m. p. 214—215°, which cannot be acetylated, quantitatively regenerates penta-acetylhemichlorogenic acid with alcohol and potassium iodide, and is converted by boiling potassium hydroxide into quinic and bromocaffeic acids. (5) The fact that only five of the six hydroxyl groups in hemichlorogenic acid can be acetylated is proved by showing by Zerewitinoff's method with magnesium methyl iodide in amyl ether that penta-acetylhemichlorogenic acid, which cannot be further acetylated even by acetyl chloride in pyridine, still contains a hydroxyl group. If hemichlorogenic acid were identical with α-quinylcaffeic acid,

$$C_6H_3(OH)_2\cdot CH{:}C(CO_2H)\cdot CO\cdot C(OH)<\begin{matrix}CH_2\cdot CH(OH)\\ CH(OH)\cdot CH_2\end{matrix}>CH\cdot OH,$$

the non-acetylated hydroxyl group would be the tertiary one, a view which is untenable, since this group in quinic acid itself is easily acetylated. (6) Chlorogenic and penta-acetylhemichlorogenic acids are not reduced by zinc dust and acetic acid, and therefore do not contain an ethylenic linking in the $\alpha\beta$-position to a carbonyl group. For these reasons and others already recorded, hemichlorogenic acid is represented by the constitution:

$$C_6H_3(OH)_2\cdot CH{:}\underset{}{C}(CO_2H)\cdot \overset{\overbrace{\qquad\qquad\quad O \qquad\qquad\quad}}{C(\underset{*}{O}H)\cdot C(OH)<\begin{matrix}CH_2\text{———}CH\\ CH(OH)\cdot CH_2\end{matrix}}>CH\cdot OH,$$

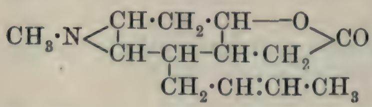
in which the * denotes the hydroxyl group which cannot be acetylated. Consequently, chlorogenic acid has the constitution :



which is in harmony with the result obtained by reducing the acid by sodium amalgam in a solution which is kept slightly acidic by the continuous addition of sulphuric acid. The product of reduction is *dihydrohemichlorogenic acid*, $C_{16}H_{20}O_9$, m. p. 167—168°, which forms a *penta-acetate*, m. p. 182°, and is decomposed by hydrochloric acid or potassium hydroxide into quinic acid and *dihydrocaffeic acid*, $C_9H_{10}O_4$, m. p. 139°. Its formation is explained by the conversion of the chlorogenic acid into hemichlorogenic acid, which, as an $\alpha\beta$-unsaturated acid, is easily reduced to the dihydro-compound. C. S.

Dioscorine. K. Gorter (*Chem. Zentr.*, 1910, ii, 1228—1229, from *Ann. Jardin Bot. Buitenzorg.*, 1909, [ii], Suppl. 3, 385—392).—From the bulbs of *Dioscorea hirsuta*, Boorsma, and later Schutte (Abstr., 1898, i, 341), isolated a crystalline alkaloid, dioscorine, $C_{13}H_{19}O_2N$. The base was isolated from the bulbs by extraction with alcohol acidified with acetic acid; it can be distilled unchanged in a vacuum. The following salts are described: *hydrobromide*, white crystals, m. p. 213—214°; *oxalate*, white prisms, m. p. 69·5—70·5°; *methiodide*, m. p. 213°; *methochloride aurichloride*, plates, m. p. 188°; *methochloride platinichloride*, orange tufts, m. p. 218°.

Dioscorine is not acted on by acetic anhydride, and it must be considered to be a tertiary base not containing an OH group. On heating with potassium hydroxide it gives a *potassium* salt, which again yields dioscorine by the action of hydrochloric acid. It must therefore be considered that dioscorine is a γ-lactone. When dioscorine is heated with concentrated potassium hydroxide at 200—250° in the presence of air, methylamine is evolved; dioscorine methiodide gives dimethylamine under similar conditions, a phenol-like substance being also formed. An acid solution of potassium permanganate is at once decolorised by dioscorine. The annexed constitution for dioscorine is suggested. N. C.



Alkaloid of Eschscholtzia Californica. Georges Brindejonc (*Bull. Soc. chim.*, 1911, [iv], 9, 97—100).—This plant contains 0·25% of a new alkaloid, ionidine. No other alkaloid is present (compare R. Fischer, Abstr., 1901, i, 743).

An alcoholic extract of the plant deposits potassium nitrate on concentration, and when extracted with warm water deposits resin. From the filtrate after defæcation with lead acetate and addition of alkali, ether extracts *ionidine*, $C_{19}H_{25}O_4N_4$, m. p. 154—156°, which crystallises in short, flattened, colourless, transparent prisms. Its solubility in cold alcohol (90°) is 0·46%, and in water 1 in 2500. The alkaloid is strongly basic, and yields bitter, very soluble, gummy salts

with acids. The *aurichloride, platinichloride*, and *mercurichloride* are all amorphous. It is precipitated from dilute solutions by iodine, picric acid, or gold chloride, and gives characteristic colour reactions with various reagents, of which the most useful are the following: sulphuric acid gives no coloration, but with sulphuric acid containing a *trace* of nitrous acid, a deep violet tint is produced, and a similar coloration is given with Fröhde's reagent. In both cases the violet tint changes to brown when kept. T. A. H.

Codeine Oxide. GUSTAV MOSSLER and ERICH TSCHEBULL (*Ber.*, 1911, **44**, 105—109).—By not too prolonged treatment with 1·5% hydrogen peroxide on the water-bath, codeine yields a bimolecular *codeine oxide*, $C_{36}H_{44}O_9N_2,7H_2O$, m. p. 200—202° (decomp.), crystallising in elongated, rectangular plates. The substance loses $6H_2O$ in a vacuum, and $7H_2O$ at 100—110°, and then has m. p. 211—215° (decomp.). It contains two atoms of active oxygen; the monohydrate has $[\alpha]_D -97·6°$ in water and $-105·9°$ in 97% alcohol, the values for the anhydrous substance being $-99·6°$ and $-107·2°$. The molecular weight is determined by the ebullioscopic method in water.

The *hydrochloride*, $C_{18}H_{21}O_4N,HCl,H_2O$, obtained by treating a hot alcoholic solution of the bimolecular oxide with hydrochloric acid, has m. p. 219—220° when anhydrous, and has $[\alpha]_D$ $-105·8°$ in water. By treating its aqueous solution with sodium carbonate. the hydrochloride yields a unimolecular *oxide*, $C_{18}H_{21}O_4N,H_2O$, m. p. 215°, $[\alpha]_D$ $-97·1°$ in water (compare Freund and Speyer, this vol., i, 76). C. S.

Aldehyde Sulphites of Vegetable Alkaloids. MARIO MAYER (*Gazzetta*, 1910, **40**, ii, 402—414).—*Brucine benzaldehyde sulphite*,

$$C_{23}H_{26}O_4N_2,H_2SO_3,C_7H_6O,$$

is prepared by treating a suspension of brucine in water with sulphur dioxide until solution is complete, and then shaking the liquid with benzaldehyde. It forms a colourless, crystalline precipitate, m. p. 125° (decomp.). The following similar compounds were prepared in the same way. The analytical figures mostly indicate an excess of alkaloid. *Brucine anisaldehyde sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_8H_8O_2$, is a white powder, which softens at 108° and decomposes at 115°. *Brucine salicylaldehyde sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_7H_6O_2$, is a colourless powder, decomposing at 120°. *Brucine heptaldehyde sulphite*,

$$C_{23}H_{26}O_4N_2,H_2SO_3,C_7H_{14}O,$$

is a white, crystalline substance, decomposing at 102°. *Brucine propaldehyde sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_3H_6O$, separates only when the solution is kept in presence of sulphuric acid; it decomposes at 135°. *Brucine acetone sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_3H_6O$, is a colourless, crystalline substance, decomposing at 190°. *Brucine benzophenone sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_{10}H_{10}O$, is prepared in alcoholic solution; it is a colourless, crystalline substance, decomposing at 120°. *Brucine acetophenone sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_8H_8O$, forms a yellow, crystalline powder, decomposing at 108°.

Brucinic acid benzaldehyde sulphite, $C_{23}H_{28}O_5N_2,H_2SO_3,C_7H_6O$, crystallises in clusters of small needles, decomposing at 122°.

Brucinic acid ethiodide, $C_{25}H_{33}O_5N_2I,H_2O$, prepared by the method

used by Moufang and Tafel (Abstr., 1899, i, 309) for the methyl derivative, is a grey mass, m. p. 205° (decomp.). It yields with sulphur dioxide and benzaldehyde a small quantity of a *substance*, m. p. 145° (decomp.), which does not contain iodine.

Berberine sulphite is obtained by acting on the hydrochloride with a saturated solution of sulphur dioxide in concentrated sodium hydrogen sulphite (compare Perkin, Trans., 1890, 57, 1097). When to a solution of the salt in the cold, benzaldehyde and alcohol are added and the liquid is treated with sulphur dioxide, *berberine benzaldehyde sulphite*, $C_{20}H_{17}O_4N,H_2SO_3,C_7H_6O$, is obtained in golden-yellow, silky needles, which become brown at 180°. *Morphine benzaldehyde sulphite*, $C_{17}H_{19}O_3N,H_2SO_3,C_7H_6O$, is a crystalline substance, m. p. 115° (decomp.). *Narcotine benzaldehyde sulphite*, $C_{22}H_{23}O_7N,H_2SO_3,C_7H_6O$, is a colourless, crystalline powder, m. p. 70° (partial decomp.). *Cocaine benzaldehyde sulphite*, $C_{17}H_{21}O_4N,H_2SO_3,C_7H_6O$, is obtained in alcoholic solution, and forms a colourless, deliquescent mass.

Quinine benzaldehyde sulphite, $C_{20}H_{24}O_2N_2,2H_2SO_3,2C_7H_6O$, prepared in alcoholic solution, is a powder which decomposes at 85°, and at ordinary temperatures and pressures evolves sulphur dioxide. *Cinchonine benzaldehyde sulphite*, $C_{19}H_{22}ON_2,2H_2SO_3,2C_7H_6O$, forms a white powder which decomposes at 90°, and loses sulphur dioxide when kept in a desiccator.

Benzaldehyde anhydrosulphites of the alkaloids are obtained when chloroform or benzene solutions of the alkaloids are treated with dry sulphur dioxide, and benzaldehyde is subsequently added. The anhydrosulphites appear as crystalline or resinous residues when the liquids are evaporated, and have properties similar to those of the sulphites. *Pilocarpine benzaldehyde anhydrosulphite*,

$$C_{11}H_{16}O_2N_2,SO_2,C_7H_6O,$$

is a colourless, crystalline substance, decomposing at 105°. The *narcotine* compound, $C_{22}H_{23}O_7N,SO_2,C_7H_6O$, is also colourless and crystalline; it decomposes at 80°. The *brucine* compound, $C_{23}H_{26}O_4N_2,SO_2,C_7H_6O$, is crystalline, and has m. p. 105° (decomp.). It dissolves readily in water, the sulphite being precipitated. The *brucinic acid compound*, $C_{23}H_{28}O_5N_2,SO_2,C_7H_6O$, is a crystalline mass, decomposing at 95°. *Strychnine*, although a monoacidic base, yields an anhydrosulphite to which the formula $C_{21}H_{22}O_2N_2,2SO_2,2C_7H_6O$ may be ascribed, although the analytical figures differ somewhat from those required by this formula. The substance is a yellow, resinous mass, m. p. 110°. (decomp.), which continually evolves sulphur dioxide. When dissolved in water it loses sulphur dioxide and benzaldehyde, and on evaporation of the solution a solid resin is obtained, m. p. 95° (decomp.), which is probably *strychnine benzaldehyde sulphite*, $C_{21}H_{22}O_2N_2,H_2SO_3,C_7H_6O$.

It is suggested that the sulphites described in this paper have the structure $C_nH_m\cdot CH<\substack{-O-\\ SO_2}>N\colon R$, N:R representing the alkaloid.

R. V. S.

Action of Sulphuryl Chloride on *s*-Dimethylpyrrole. U. Colacicchi (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 645—648).—Sulphuryl chloride (2 mols.) reacts with 2 : 5-dimethylpyrrole in

ethereal solution at 0°. The liquid, after remaining for two days at the ordinary temperature, was treated with ice, and the residue from the ethereal solution was subjected to steam distillation. No distillate was obtained, but the aqueous residue in the distilling vessel deposited crystals on cooling, from which, by the aid of solvents, two substances were obtained in very small quantity. One of these did not melt at 300°; it behaved as an acid, and gave an unstable *silver* salt, The other substance crystallised in stellate clusters of needles, m. p. 228° (decomp.), had the composition $C_6H_3O_2NCl_2$, and the reactions of an aldehyde. It reduced ammoniacal silver solution, gave a white *substance* with ammonia, yielded a p-*nitrophenylhydrazone*, m. p. 237°. and formed a naphthacinchoninic *derivative*, m. p. 265°, with pyruvic acid and β-naphthylamine. For these reasons the substance is assigned the structure of 3 : 4-*dichloro*-2 : 5-*dialdehydopyrrole*,

$$\begin{matrix}\mathrm{CCl{:}C(CHO)} \\ | \\ \mathrm{CCl{:}C(CHO)}\end{matrix}\!\!>\!\mathrm{NH},$$

whilst the acid above-mentioned is probably the corresponding dibasic acid, 3 : 4-*dichloropyrrole*-2 : 5-*dicarboxylic acid.* R. V. S.

The Ferriammines. GIUSEPPE A. BARBIERI and G. PAMPANINI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 591—594).—Ferric thiocyanate yields with certain organic bases crystalline compounds containing for every molecule of thiocyanate three molecules of the base. They have a constitution similar to that of the tripyridinechromium chloride of Pfeiffer (Abstr., 1907, i, 872). *Tripyridineferric thiocyanate*, $Fe{(SCN)_3 \atop (C_5NH_5)_3}$, is prepared by mixing the calculated quantities of ferric thiocyanate and pyridine in aqueous or, better, in ethereal solution. It forms dark green crystals, which are insoluble in water, but are soluble in various organic solvents with production of either red or violet solutions. *Triquinolineferric thiocyanate*, $Fe(SCN)_3(C_9H_7N)_3$, is similar to the pyridine derivative; it forms crystals which are almost black. *Triantipyrineferric thiocyanate*, $Fe(SCN)_3(C_{11}H_{12}ON_2)_3$, forms red crystals. R. V. S.

Rupture of the Pyridine Ring. FRITZ REITENSTEIN and WILHELM BREUNING (*J. pr. Chem.*, 1911, [ii], **83**, 97—130).—Vongerichten (Abstr., 1900, i, 51; compare Spiegel, *ibid.*, 1901, i, 752) has shown that 1-chloro-2 : 4-dinitrobenzene and pyridine form an additive compound containing a quinquevalent nitrogen atom, and Zincke (Abstr., 1904, i, 448, 921; 1905, i, 241, 923) has proved that this additive compound reacts with primary and secondary arylamines, yielding 2 : 4-dinitroaniline and derivatives of glutaconaldehyde of the type NHPhCl:CH·CH:CH·CH:CH·NHPh, due to the rupture of the pyridine ring (compare Dieckmann, Abstr., 1905, i, 411). It is now shown that other substances containing negative groups can form quaternary ammonium salts with pyridine, for example, diaryloxaliminochlorides, benzanilideimidechloride, phosphorus pentachloride, etc., and that these additive compounds react with primary arylamines, producing a rupture of the pyridine ring and the formation of red dyes of the same type as those described by Zincke. It has

not been found possible to isolate definite additive compounds in all the cases studied, but the subsequent formation of a red dye by the action of an amine is regarded as proof of the formation of an additive compound between the pyridine and the compound containing the negative groups.

Di-o-tolyloxaliminochloride-pyridinium chloride,

$$C_5NH_5Cl{\cdot}C({:}N{\cdot}C_6H_4Me){\cdot}CCl{:}N{\cdot}C_6H_4Me,$$

obtained by warming a mixture of anhydrous pyridine and di-*o*-tolyloxalimino chloride (Bauer, Abstr., 1907, i, 603) with toluene, extracting the crude product with hot acetone, and crystallising the residue three times from methyl alcohol, forms intensely yellow-coloured plates, m. p. 180°. When boiled with water, acids, or alkalis, it is decomposed, and yields carbylamine derivatives. Its solution in concentrated sulphuric acid has a blood-red colour, and when poured into water yields oxalyl-*o*-toluidide. The *platinichloride*,

$$2C_{21}H_{19}N_3Cl_2,H_2PtCl_6,$$

forms orange-yellow crystals decomposing at 210—212°.

Diphenyloxaliminochloride-pyridinium chloride,

$$C_5NH_5Cl{\cdot}C({:}NPh){\cdot}CCl{:}NPh,$$

prepared in a similar manner from pyridine and diphenyloxalimino chloride, crystallises from methyl alcohol in yellow plates, which turn brown at 200° and melt at 203°.

When the di-*o*-tolyl derivative is warmed for a short time with an alcoholic solution of *p*-toluidine, Zincke's glutacondi-*p*-toluidide hydrochloride is obtained, and with an alcoholic solution of β-naphthylamine the corresponding β-naphthalide. The additive compound of pyridine and bezanilidedi-imidechloride (Wallach, this Journ., 1877, ii, 187) could not be isolated, but by the action of aniline, Zincke's dianilide was obtained, together with anilinobenzylideneaniline (Bernthsen, *Annalen*, 1877, **184**, 353).

A mixture of carbodiphenylimide (Schall, Abstr., 1895, i, 42), pyridine hydrochloride, and *p*-toluidine yields Zincke's *p*-toluidide, and a mixture of phosphorus pentachloride, pyridine, and aniline gives the corresponding anilide.

Pyridine dibromide and potassium cyanide react, yielding the product obtained by König from pyridine cyanogen bromide, and this with aniline yields the glutacondianilide. For the preparation of the anilide it is not necessary to isolate the intermediate compound.

Experiments on the chlorination of pyridine have been carried out. By chlorinating in dry ethereal solution, an unstable, colourless derivative is formed, which readily loses chlorine and reacts explosively with ether, alcohol, or aniline. With water, it yields dichloropyridine hydrochloride, $C_5NH_3Cl_2,HCl,H_2O$, which turns brown at 160° and melts at 168° (decomp.).

The product of chlorination yields a precipitate with mercuric chloride solution, and when this precipitate is decomposed by boiling with concentrated potassium chloride solution, dichloropyridine distils over, and this forms a *mercurichloride*, $C_5NH_5Cl_4Hg_2$, which crystallises from methyl alcohol in brilliant, colourless needles, m. p. 190°.

When pyridine is chlorinated without the addition of a solvent, but in the presence of zinc chloride or sea-sand, and at low temperatures,

a white precipitate is first obtained, but this re-dissolves, and ultimately a dark brown, viscous product is formed. The behaviour of the various chlorinated products towards primary amines has been studied. The white precipitate obtained by chlorinating pyridine in dry ethereal solution when distilled under reduced pressure gave fractions which did not yield dyes with primary arylamines. Similarly, the distillates obtained from the dark viscous liquid, formed by chlorinating pyridine in the presence of zinc chloride, did not give colorations with β-naphthylamine, neither did tri-, tetra-, and penta-chloropyridines. On the other hand, the white precipitate when left in contact with ether and the air underwent partial decomposition, and then reacted with aromatic bases, yielding red dyes of varying composition, and the undistilled dark viscid oil gave a red product with p-toluidine melting at 197—198°, with β-naphthylamine a *compound*, $C_{35}H_{27}N_3$, in the form of strongly electrical, dark red needles, m. p. 245°, and with α-methyldihydroindole a product in the form of a cochineal-red precipitate, which has not been analysed.

The *cis*- and *trans*-tolane dichlorides and phosphorus trichloride do not yield dyes with mixtures of pyridine and an aromatic amine.

A list of the various amines which react with the chlorinated pyridine is given, together with the colours produced. The characteristic line in the spectra of the various coloured condensation products is also given. J. J. S.

Condensation Product of Ethyl Phthalimino*iso*butyrylmalonate. SIEGMUND GABRIEL (*Ber.*, 1911, 44, 70—91. Compare this vol., i, 212).—The yellow by-product obtained by the interaction of ethyl sodiomalonate and α-phthalimino*iso*butyryl chloride in benzene becomes the main product when $1\frac{1}{2}$ mols. of ethyl sodiomalonate are employed. (In the former method of preparation [*loc. cit.*] the yellow by-product is mixed with a colourless *substance*, m. p. 168—168·5°, which is shown to be *α-phthalimino*iso*butyric anhydride* by its formation also from α-phthalimino*iso*butyric acid and its chloride at 170°.) The same *substance*, $C_{16}H_{15}O_4N$, yellow prisms, m. p. 176—177°, is produced when ethyl α-phthalimino*iso*butyrylmalonate is boiled with sodium in benzene. It no longer yields phthalic acid by hydrolysis with hydrochloric acid, and its behaviour, described below, points to the constitution of an ethyl benzoylenedimethylpyrrolonecarboxylate (I), obtained in accordance with the equation:

$$C_6H_4{<}{}^{CO}_{CO}{>}N\cdot CMe_2\cdot CO\cdot CH(CO_2Et)_2 =$$

$$\begin{array}{l} C_6H_4\cdot C{:}C(CO_2Et) \\ CO{-}N\cdot CMe_2 \end{array}{>}CO + CO_2 + C_2H_6O.$$

When the ester is hydrolysed by equal volumes of water and concentrated sulphuric acid, it yields 3-*keto*-2 : 2-*dimethyl*-2 : 3-*dihydropyrrole*-5-o-*benzoic acid*, $\begin{array}{l} CMe_2\cdot NH \\ CO{-}CH \end{array}{\gg}C\cdot C_6H_4\cdot CO_2H$ (II) [*hydrobromide*, $C_{13}H_{13}O_3N,HBr,H_2O$, m. p. 200° (decomp.)], which readily suffers ring closure at its m. p., 191° (decomp., rapidly heated), or by prolonged boiling

with mineral acids, yielding *benzoylenedimethylpyrrolone* (III),

$$\begin{matrix} C_6H_4\cdot C{=}CH \\ | \qquad\quad | \\ CO{-}N\cdot CMe_2 \end{matrix}\!\!>CO,$$

m. p. 125—126°. This is reconverted into (II) by warm alkalis, and forms *benzoylene-4-bromodimethylpyrrolone* (IV), $\begin{matrix} C_6H_4\cdot C{=}CBr \\ CO{-}N\cdot CMe_2 \end{matrix}\!\!>CO$, m. p. 224—225°, with bromine in glacial acetic acid. Substance (III) is reduced by hydriodic acid and red phosphorus to *benzoylenedimethylpyrrolidone* (VII), $\begin{matrix} C_6H_4\cdot CH\cdot CH_2 \\ CO{-}N{=}CMe_2 \end{matrix}\!\!>CO$, m. p. 172—173°, which is also formed from (I) and from (II) by the same reducing agent. Substance (VII), unlike (III), is not ruptured by warm alkalis, forms a *phenylhydrazone*, m. p. 215—217·5°, and an *oxime*, 220—221·5°, and yields a *nitro*-compound, $C_{13}H_{12}O_4N_2$, m. p. 172—173° (decomp.), with warm fuming nitric acid.

When substance (III) is treated with fuming nitric acid below 20°, it is converted into *benzoylene-4-nitrodimethylpyrrolone* (V),

$$\begin{matrix} C_6H_4\cdot C{:}C(NO_2) \\ CO{-}N{-}CMe_3 \end{matrix}\!\!>CO,$$

m. p. 264—265° (decomp.), which is reduced by hydriodic and glacial acetic acids, partly to substance (VII), partly to *benzoylene-4-aminodimethylpyrrolone* (VI), $C_{13}H_{12}O_2N_2$, orange-red prisms, m. p. 212°.

By treatment with methyl-alcoholic hydrogen chloride, substance (II) yields the *hydrochloride*, m. p. 199—199·5° (decomp.), of its methyl ester, an aqueous solution of which is reconverted into (II) by an excess of sodium carbonate. Bromine in glacial acetic acid converts (II) into *4-bromo-3-keto-2 : 2-dimethyl-2 : 3-dihydropyrrole-5-o-benzoic acid* (VIII), $CO_2H\cdot C_6H_4\cdot C\!\!<\!\begin{matrix} CBr\cdot CO \\ NH\cdot CMe_2 \end{matrix}$, m. p. 223° (slowly heated), which is re-converted into (II) and another (unexamined) substance by 20% potassium hydroxide on the water-bath; is almost unattacked by aniline at 150° (substance IV is produced in this experiment), and reacts with alcoholic ammonia at 100° to form a *substance*, $C_{13}H_{12}O_2N_2$ (XI), m. p. 303—304°, and with methylamine to form a *substance*, $C_{13}H_{11}MeO_2N_2$ (XIII), m. p. 222—223°, the constitutions of which are discussed below.

By the action of cold hydrochloric acid and potassium nitrite, substance (II) is changed into *1 : 4-dinitroso-3-keto-2 : 2-dimethyl-2 : 3-dihydropyrrole-5-o-benzoic acid* (IX),

$$CO_2H\cdot C_6H_4\cdot C\!\!<\!\begin{matrix} C(NO)\cdot CO \\ N(NO)\cdot CMe_2 \end{matrix},$$

m. p. about 160° (decomp.), which is converted by warm aqueous sodium carbonate into *4-nitroso-3-keto-2:2-dimethyl-2:3-dihydropyrrole-5-o-benzoic acid* (X), $CO_2H\cdot C_6H_4\cdot C\!\!<\!\begin{matrix} C(NO)\cdot CO \\ NH{-}CMe_2 \end{matrix}$, m. p. 182° (decomp.). This substance (X), which is obtained more conveniently by treating (II) with 50% alcohol, 50% acetic acid, and potassium nitrite, forms a *silver* salt, $C_{13}H_{11}O_4N_2Ag,H_2O$, decomp. 260—270°, and is

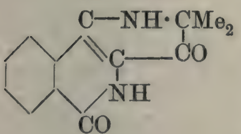
regarded as containing the nitroso-group in position 4 for the following reasons. It yields substance (VIII) with alcoholic bromine, is converted by nitric acid, D 1·2, into the 4-*nitro-acid* (X*a*),

$$CO_2H\cdot C_6H_4\cdot C\Big\langle\begin{matrix}C(NO_2)\cdot CO\\ NH\text{———}CMe_2\end{matrix},$$

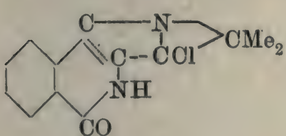
m. p. 262—264° (decomp) (which is changed into V by boiling acetic anhydride), and is reduced, as also is (X*a*), by hydriodic and glacial acetic acids to substance (XI). This substance forms yellow crystals, gives a bluish-green fluorescent solution in boiling water, and a malachite-green solution in concentrated sulphuric acid, from which a blue powder is precipitated by the addition of water. Its insolubility in aqueous ammonia proves the absence of a carboxyl group, and its formation from substances (VIII) and (X) is explained by the formation of the same (unisolated) intermediate compound,

$$CO_2H\cdot C_6H_4\cdot C\Big\langle\begin{matrix}NH\text{———}CMe_2\\ C(NH_2)\cdot CO\end{matrix},$$

from which substance (XI) (annexed constitution) is obtained by the elimination of water. The substance, which is called *gyrolone*, is isomeric with substance (VI); in fact, (VI) can be converted into gyrolone by the action of alcoholic potassium hydroxide and treatment of the product with aqueous ammonium chloride. That the solubility of gyrolone in alkali hydroxides is due to the presence of the acidic imino-group is indicated by the fact that substance (XIII), which contains NMe, is insoluble in these solvents; (XI) is converted into (XIII) by methyl-alcoholic potassium hydroxide and methyl iodide. By treatment with phosphoryl chloride on the water-bath, gyrolone is converted into a *substance*, $C_{13}H_{11}ON_2Cl$, pale yellow needles, which sublimes under diminished pressure, has m. p. 196°, develops a malachite-green coloration in concentrated sulphuric acid, is insoluble in aqueous ammonia, but dissolves in alkali hydroxides;



these properties point to the annexed constitution. The substance, which is called *chlorogyrilone*, is converted by methylation into the same *N-methyl* homologue, $C_{13}H_{10}MeON_2Cl$, m. p. 128—128·5°, as is obtained by the action of phosphoryl chloride on substance (XIII).



By reduction with hydriodic acid, b. p. 127°, and red phosphorus, chlorogyrilone is converted into a *base*, $C_{13}H_{16}O_2N_2$, citron-yellow needles, m. p. 196—198°, which loses H_2O in a vacuum, yielding *dihydrogyrilone*, $C_6H_4\Big\langle\begin{matrix}\text{————}C\cdot NH\\ CO\cdot NH\cdot \overset{\|}{C}\cdot CH_2\end{matrix}\Big\rangle CMe_2$, m. p. 190—198°, clarifying completely at 210°, a solution of which in dilute sulphuric acid reduces gold and silver salts and also Fehling's solution. The product of the oxidation, $C_{13}H_{12}ON_2$, m. p. 212° (decomp.) (the *hydrochloride*, *chromate*, *aurichloride*, and *platinichloride* are mentioned), is obtained best by oxidising a solution of dihydrogyrilone or of its hydrate in

hydrochloric acid with an excess of bromine; the substance probably has the constitution $C_6H_4<\begin{matrix}\text{————}\cdot C\cdot N\text{—}\\ CO\cdot NH\cdot C\cdot CH\end{matrix}>CMe_2$.

When a solution of gyrilone in fuming hydrochloric acid is heated at 135° for two hours and the resulting green powder is distilled in a vacuum, a *substance*, $C_{15}H_{12}ON_2$, isomeric with gyrilone, but devoid of basic properties, is obtained. It crystallises in yellow leaflets, melts and decomposes above 300°, and sublimes when heated carefully on a watch-glass; its constitution is as yet unascertained. C. S.

Transformation of Naphthalimide into Naphthastyril. ELIE E. PISOVSCHI (*Bull. Soc. chim.*, 1911, [iv], 9, 86—88).—As the processes described by Francesconi and Recchi (Abstr., 1901, i, 721), and by Ullmann and Cassirer (Abstr., 1910, i, 201), do not give good yields, the following new process, which gives a quantitative yield, has been devised.

Naphthalimide (40 grams) dissolved in 600 c.c. of sodium hydroxide solution (3%) is treated at 40° with 480 c.c. of sodium hypochlorite solution containing 5·5% by weight of active chlorine, and the mixture warmed for thirty minutes at 65°. To this, 172 c.c. of sodium hydrogen sulphite solution (30%) are added, and the cooled mixture filtered and the filtrate diluted to 2750 c.c. From this, naphthastyril is precipitated in three fractions by (*a*) adding acetic acid, (*b*) adding dilute sulphuric acid, and (*c*) concentrating the mother liquors. The product may be crystallised from acetic acid.

Dilute solutions of naphthastyril in organic solvents show a green fluorescence. The solution in sulphuric acid is yellow (compare Ekstrand, Abstr., 1886, 715; 1889, 52). T. A. H.

Diacetyl. Diacetylmonophenylhydrazones and their Condensations. OTTO DIELS and ANTON KOLLISCH (*Ber.*, 1911, 44, 263—268. Compare Abstr., 1903, i, 400; 1905, i, 509; 1907, i, 480; 1909, i, 455).—Although diacetylphenylhydrazone is not decomposed when boiled with hydrochloric acid, the corresponding phenylmethylhydrazone is readily transformed into 1-acetyl-2-methylindole when well shaken with warm hydrochloric acid. The phenylhydrazone and the phenylmethylhydrazone condense readily with ethyl oxalate, yielding hydrazones of ethyl diacetyloxalate, but so far it has not been found possible to remove the hydrazo-group from the condensation products.

Diacetylphenylmethylhydrazone, COMe·CMe:N·NMePh, is formed, together with a small amount of the corresponding osazone, by the action of phenylmethylhydrazine on diacetyl in acetic acid solution. It is a deep yellow oil, has b. p. 154—155°/14 mm. (corr.) and D^{20} 1·0809, and condenses with ethyl oxalate in the presence of dry sodium ethoxide and anhydrous ether, yielding the *phenylmethylhydrazone* of *ethyl diacetyloxalate*,

$$CO_2Et\cdot CO\cdot CH_2\cdot CO\cdot CMe:N\cdot NMePh,$$

which crystallises from methyl alcohol in red needles, m. p. 88° after

sintering. The corresponding *phenylhydrazone*, $C_{14}H_{16}O_4N_2$, crystallises from alcohol in golden-yellow plates, m. p. 148—149° (corr.).

1-*Acetyl-2-methylindole*, $C_6H_4<\begin{smallmatrix}CH\\NMe\end{smallmatrix}>CAc$, crystallises from light petroleum in stout, colourless plates, m. p. 72°, and yields a *picrate*, $C_{17}H_{14}O_8N_4$, in the form of long, orange needles, m. p. 117°, and a *phenylhydrazone*, $C_{17}H_{17}N_3$, in the form of long, nearly colourless, needles, m. p. 117—118°. J. J. S.

Isatinanils. IV. Cases of Desmotropism. RUDOLF PUMMERER [with F. GRUBE] (*Ber.*, 1911, 44, 338—345. Compare Abstr., 1910, i, 511).—Isatin-2-anil crystallises from benzene in brownish-violet prisms, m. p. 126°, but is precipitated by sodium carbonate from solutions of its salts in brown, crystalline flakes, which crystallise from dilute alcohol in large, yellowish-brown plates, m. p. 126°. At about 110°, partial transference into the violet form is observed. The two modifications are not identical, the yellow leaflets representing isatin-2-anil, $C_6H_4<\begin{smallmatrix}NH\\CO\end{smallmatrix}>C:NPh$, and the violet prisms, isatin-2-anilide, $C_6H_4<\begin{smallmatrix}N\\CO\end{smallmatrix}>C\cdot NHPh$. The violet form immediately gives red solutions; the yellow form yields yellowish-brown solutions in anhydrous solvents at low temperatures, which soon become red.

1-*Methylisatin-2-anil*, $C_6H_4<\begin{smallmatrix}NMe\\CO\end{smallmatrix}>C:NPh$, is obtained by the action of sodium methoxide and methyl iodide; it crystallises in yellowish-red prisms, m. p. 132°, and is hydrolysed by acids to 1-methylisatin and aniline.

Isatin-2-methylanilide, $C_6H_4<\begin{smallmatrix}N\\CO\end{smallmatrix}>C\cdot NMePh$, prepared by the interaction of isatin chloride with methylaniline in benzene solution, crystallises in long, bluish-violet plates, m. p. 103—104°. It is hydrolysed into isatin and methylaniline.

In the case of both isomerides the introduction of methyl causes a deepening of the colour. There is a considerable difference in the basicity of the two forms; the methyl-anil does not react with concentrated sodium hydrogen sulphite solution, whereas the methyl-anilide forms almost quantitatively a sparingly soluble bisulphite compound.

A similar isomerism has been studied in the case of thioindigo-scarlet-2-anil, which is red, and thioindigoscarletanilide, which is greenish-brown (compare following abstract). In this example the anil form is more stable, and has been studied in solution. It is best converted into the anilide by means of acids, boiling with pyridine being the most satisfactory method of effecting the reverse change.

E. F. A.

Indirubinanils: Substances with Reactive Carbon Double Bonds. RUDOLF PUMMERER [with MAXIMILIAN GOETTLER] (*Ber.*, 1911, 44, 346—356. Compare preceding abstract; also Abstr., 1910, i, 511). —Isatin-2-anil reacts in alkaline solution with indoxyl, forming

indirubin-2-anil, in which the anil residue, being no longer in the neighbourhood of a CO group, is firmly fixed. In a similar manner indirubin-*p*-dimethylamino-2-anil and the corresponding sulphur compound have been prepared: both are blue dyes.

Thioindigo-scarlet-*p*-dimethylamino-2-anil on prolonged heating with 1% hydrogen chloride is decomposed quantitatively into aminodimethylaniline and thioindigo-scarlet, but the indirubin compound under similar treament only gives small quantities of indirubin, the main part being converted into a reddish-brown compound, $C_{15}H_{11}O_2N$, which has not been further investigated.

Indirubin-2-anil is decomposed by indoxyl into an indigo dye and *oxindoleanil*, $C_6H_4<\substack{CH_2\\NH}>C:NPh$. The reaction is quantitative, and takes place rapidly in hot dilute acetic acid.

The carbon double bond in indirubinanil is opened by the action of phenylhydrazine, and isatin-2-phenylhydrazone is formed.

Oxidoleanil forms colourless flakes, m. p. 90—92°; it rapidly becomes violet on exposure to moist air. The *hydrochloride* forms short, lancet-shaped crystals, m. p. 219—220°. When warmed with nitrosobenzene, isatindianil is formed.

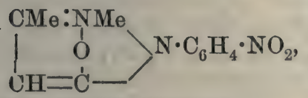
The brown modification of *thioindigo-scarlet*-2-*anilide* [3(1′)-*thionaphthenyl*-ψ-*indole*-2-*anilide*], $C_6H_4<\substack{S\\CO}>C:C<\substack{C_6H_4\\C(NHPh)}>N$ (see preceding abstract), formed by the interaction of isatin-2-anil with 2-hydroxythionaphthen, crystallises in long, narrow, brown prisms, m. p. 226—227°. The red *anil* form, $C_6H_4<\substack{S\\CO}>C:C<\substack{C_6H_4\\C(:NPh)}>NH$, prepared by boiling the brown form in dry pyridine, crystallises in carmine-red prisms with a coppery lustre.

3(1′)-*Thionaphthenyl*-ψ-*indole*-p-*dimethylamino*-2-*anil* crystallises in lustrous, violet-black plates, m. p. 220—221°.

Indirubin-p-*dimethylamino*-2-*anil* forms bluish-violet plates, m. p. 257—258°. The *sulphate* forms rectangular violet-black plates of metallic lustre, m. p. 255—256°. E. F. A.

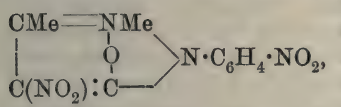
1-Nitro- and 1-Amino-derivatives of Antipyrine, Thiopyrine, and Anilopyrine. August Michaelis [with Walter Graff, Richard Gesing, and Heinrich Boie] (*Annalen*, 1911, **378**, 293—351).—A previous attempt to prepare *p*-nitroantipyrine from methyl iodide and 5-chloro-1-*p*-nitrophenyl-3-methylpyrazole failed, because the two reagents yielded an iodo-*p*-nitrophenylmethylpyrazole methiodide, from which the *p*-nitroantipyrine could not be obtained by the action of alkalis or of silver oxide (Michaelis and Behn, Abstr., 1900, i, 693). Success has now been attained by treating the chloro-*p*-nitrophenylmethylpyrazole with an excess of methyl sulphate at 110° and treating the neutralised aqueous solution of the methosulphate with potassium iodide, whereby 5-*chloro*-1-p-*nitrophenyl*-3-*methylpyrazole methiodide*, $\substack{CH\text{———}CMe\\ \| \\ CCl\cdot N(C_6H_4\cdot NO_2)}>N,MeI$, yellow crystals, m. p. 196°, is obtained; an aqueous solution of this methiodide, by treatment with

silver oxide and subsequent evaporation, yields p-*nitroantipyrine* (1-p-*nitrophenyl*-2 : 3-*dimethyl*-5-*pyrazolone*) (annexed formula), yellow prisms, m. p. 132°. *p*-Nitroantipyrine, which can also be prepared, although less satisfactorily, by warming an aqueous solution of the preceding methiodide with the calculated quantity of hydroxylamine hydrochloride and sodium carbonate, forms a *hydrochloride*,



$$C_{11}H_{11}O_3N_3,HCl,$$

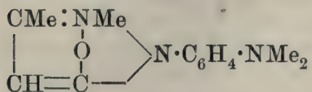
m. p. 191·5°, which is decomposed by water; *platinichloride*, large, red crystals; *hydriodide*, m. p. 163° (decomp.), and *picrate*, m. p. 101°. The methine hydrogen atom in position 4 exhibits its customary activity. Thus, by treatment with sodium nitrite in glacial acetic acid, *p*-nitroantipyrine yields p-*nitro*-4-*nitrosoantipyrine*, a green, crystalline powder, which becomes yellow at 176° and has m. p. 188—189°. p-4-*Dinitroantipyrine* (annexed formula), colourless needles, m. p. 276°, is prepared by the action of nitric and sulphuric acids on antipyrine, by treating *p*-nitroantipyrine with nitric acid, or by heating 5-*chloro*-4-*nitro*-1-p-*nitrophenyl*-3-*methylpyrazole*, m. p. 181° (obtained by the action of nitric and sulphuric acids on 5-chloro-1-phenyl-3-methylpyrazole) with methyl sulphate at 115—120° and decomposing the resulting methosulphate with sodium carbonate.



4-*Bromo*-p-*nitroantipyrine*, obtained from the nitroantipyrine and bromine in chloroform solution, has m. p. 173°. By reduction with tin and hydrochloric acid, *p*-nitroantipyrine yields *p*-aminoantipyrine, m. p. 210°, which does not condense with aldehydes; its *hydrochloride*, $C_{11}H_{13}ON_3,2HCl$, has m. p. 220° (decomp.). The *acetyl* derivative, m. p. 221°, forms 4-*nitroso*-p-*acetylaminoantipyrine*, green needles, m. p. 237° (decomp.), with potassium nitrite in acetic acid solution, and 4-*bromo*-p-*acetylaminoantipyrine*, m. p. 240°, with bromine in chloroform. p-*Benzoylaminoantipyrine*, m. p. 261°, yields 4-*nitroso*-p-*benzoylaminoantipyrine*, m. p. 214°, and 4-*bromo*-p-*benzoylaminoantipyrine*, m. p. 237°, by similar processes. p-*Benzenesulphonylaminoantipyrine*, m. p. 251°, obtained from *p*-aminoantipyrine and benzenesulphonyl chloride in alcoholic solution, yields a 4-*nitroso*-compound, m. p. 211° (decomp.), and a 4-*bromo*-compound, m. p. 235°. p-4-*Diaminoantipyrine*, m. p. 279°, obtained by reducing dinitroantipyrine by tin and hydrochloric acid, forms a *diacetyl* derivative, m. p. 291°, which has only a slight antipyretic action.

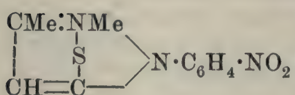
The following compounds of *m*-nitroantipyrine and of *o*-nitroantipyrine are obtained, in the main, by processes similar to those mentioned above. 5-*Chloro*-1-m-*nitrophenyl*-3-*methylpyrazole methiodide*, m. p. 222°, yellow needles. m-*Nitroantipyrine*, m. p. 98°, yellow needles, forms a *hydrochloride*, m. p. 188°, which is decomposed by water; *platinichloride*, $2C_{11}H_{11}O_3N_3,H_2PtCl_6,2H_2O$, m. p. 140°; *hydriodide*, m. p. 171°; *picrate*, m. p. 165°, and *nitrate*, m. p. 143°. m-*Nitro*-4-*nitrosoantipyrine*, green crystals, decomp. 165°, complete at 188—190°. m-4-*Dinitroantipyrine*, prepared from *m*-nitroantipyrine and nitric acid with cooling, decomposes at 203°. 4-*Bromo*-m-*nitro*-

antipyrine, m. p. 184°. m-*Aminoantipyrine*, m. p. 148°, does not react with aldehydes, phenylthiocarbimide, or carbon disulphide; it forms a *hydrochloride*, $C_{11}H_{13}ON_3,2HCl$, m. p. 228°, which is very unstable; *platinichloride*, $2C_{11}H_{13}ON_3,H_2PtCl_6,2H_2O$, decomp. above 200°, and an *acetyl* derivative, $C_{13}H_{15}O_2N_3,H_2O$, m. p. 127° (hydrated), 167° (anhydrous), which has only a slight antipyretic action. 4-*Bromo*-m-*acetylaminoantipyrine* has m. p. 217°. m-*Benzoylaminoantipyrine* has m. p. 119°. m-*Dimethylaminoantipyrine* (*ψ-pyramidone*) (annexed formula), obtained by heating *m*-aminoantipyrine and methyl sulphate nearly at the b. p. for half an hour and basifying the aqueous solution of the resulting methosulphate, is an oil which forms a *platinichloride*, reddish-brown needles, m. p. 270° (decomp.). *m*-4-*Diaminoantipyrine*, m. p. 170°, forms a *hydrochloride*, $C_{11}H_{14}ON_4,2HCl$, m. p. 245°, and a *diacetyl* derivative, m. p. 273°.



5-*Chloro*-1-o-*nitrophenyl*-3-*methylpyrazole methiodide*, m. p. 183°, yellow prisms, is converted by silver oxide in the preceding manner into o-*nitroantipyrine*, m. p. 188°, which forms a *hydrochloride*, m. p. 201°, and *platinichloride*, $2C_{11}H_{11}O_2N_3,H_2PtCl_6,2H_2O$, m. p. 133° (hydrated), decomp. above 300° (anhydrous). o : 4-*Dinitroantipyrine*, white needles, has m. p. 244°. o-*Aminoantipyrine* has m. p. 165°.

2 : 5-*Thio*-1-m-*nitrophenyl*-2 : 3-*dimethylpyrazolone* (m-*nitrothiopyrine*) (annexed formula), m. p. 204°, yellow leaflets, obtained by treating a suspension of 5-chloro-1-*m*-nitrophenyl-3-methylpyrazole methiodide in chloroform with a concentrated alcoholic solution of potassium sulphide (the use of aqueous solutions is to be avoided, since the hydrogen sulphide liberated reduces the nitro-group to the amino-group), forms a *hydrochloride*, $C_{11}H_{11}O_2N_3S,HCl$, m. p. 147°, which is decomposed by water, *platinichloride*, m. p. 225°, *hydriodide*, m. p. 185°, *methiodide*, m. p. 209°, and *trioxide*, $C_{11}H_{11}O_5N_3S$, m. p. above 350°, the last being obtained by passing chlorine through a hot aqueous solution of the nitrothiopyrine.



5-*Methylthiol*-1-m-*nitrophenyl*-3-*methylpyrazole* (m-*nitro-ψ-thiopyrine*),

$$\begin{matrix} CMe{=\!=\!=}N \\ CH{:}C(SMe) \end{matrix}\!\!>\!N{\cdot}C_6H_4{\cdot}NO_2,$$

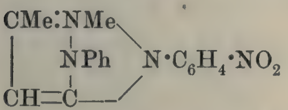
m. p. 84°, white needles, is obtained by carefully heating *m*-nitrothiopyrine methiodide under reduced pressure; by oxidation by potassium permanganate in glacial acetic acid, it yields the *sulphone*,

$$C_{11}H_{11}O_4N_3S,$$

m. p. 135°. m-*Aminothiopyrine*, m. p. 199°, obtained by reducing the nitrothiopyrine by tin and hydrochloric acid, forms a *hydrochloride*, m. p. 226°, and *platinichloride*, an amorphous, red powder. The following compounds are obtained by methods similar to the preceding: 2 : 5-*thio*-1-o-*nitrophenyl*-2 : 3-*dimethylpyrazolone* (o-*nitrothiopyrine*), m. p. 190°, blood-red-crystals, forms a *hydrochloride*, m. p. 125°, *platinichloride*, decomp. 230°, *hydriodide*, m. p. 152°, *methiodide*, m. p. 181°, and *trioxide*, m. p. 298°. o-*Nitro-ψ-thiopyrine* and its sulphone have m. p. 61° and 160° respectively. o-*Aminothiopyrine*,

m. p. 172°, forms a *platinichloride*, decomp. 300°. 2 : 5-*Thio*-1-p-*nitrophenyl*-2 : 3-*dimethylpyrazolone* (p-*nitrothiopyrine*), m. p. 241°, red crystals, is obtained by treating a hot aqueous solution of 5-chloro-1-*p*-nitrophenyl-3-methylpyrazole methiodide with concentrated aqueous sodium sulphide ; it forms a *hydrochloride*, m. p. 175°, *methiodide*, m. p. 196°, and *trioxide*, decomp. above 370°. *p*-Nitro-ψ-thiopyrine (Michaelis and Besson, Abstr., 1904, i, 780) forms a *hydrochloride*, m. p. 85°, and a *sulphone*, m. p. 154° ; 4-*bromo*-p-*nitro*-ψ-*thiopyrine* has m. p. 120°. p-4-*Dinitrothiopyrine*, m. p. 240°, yellow crystals, obtained in a similar manner to the dinitroantipyrine, forms a *methiodide*, m. p. 154—155°, which by heating under reduced pressure yields the *dinitro*-ψ-*thiopyrine*, m. p. 123° ; the corresponding *sulphone* has m. p. 177°. p-*Aminothiopyrine*, m. p. 255—256°, obtained by the reduction of *p*-nitrothiopyrine, forms a *hydrochloride*, $C_{11}H_{13}N_3S,2HCl$, an *acetyl* derivative, m. p. 271°, and *benzoyl* derivative, m. p. 265°. p-*Amino*-ψ-*thiopyrine*, m. p. 132°, white leaflets, obtained by the reduction of *p*-nitro-ψ-thiopyrine, forms a *hydrochloride*, $C_{11}H_{13}N_3S,2HCl$, m. p. 221°, and an *acetyl* derivative, m. p. 137°. p-4-*Diaminothiopyrine*, m. p. 207°, obtained in a similar manner to the diaminoantipyrine, forms a *diacetyl* derivative, m. p. 273°. p-4-*Diamino*-ψ-*thiopyrine*, m. p. 115°, white needles, is obtained by the reduction of the dinitro-ψ-thiopyrine ; its *diacetyl* derivative has m. p. 235°.

2 : 5-endo*Anilo*-1-m-*nitrophenyl*-2 : 3-*dimethylpyrazole* (m-*nitroanilopyrine*) (annexed formula), m. p. 110°, reddish-brown needles, is obtained by heating 5-chloro-1-*m*-nitrophenyl-3-methylpyrazole methiodide and aniline (2 mols.) at 125° for two hours. It reduces Fehling's solution and silver salts, and is a strong base; the *hydriodide*, m. p. 166°, *platinichloride*, *picrate*, *thiocyanate*, m. p. 168°, *methiodide*, m. p. 222°, *ethiodide*, m. p. 176°, and *propiodide*, m. p. 130°, are described. By treatment with benzoyl chloride in benzene, *m*-nitroanilopyrine forms a *benzoyl chloride*, which is isolated as the *platinichloride*, $2(C_{17}H_{16}O_2N_4,C_6H_5\cdot COCl)PtCl_4$, m. p. 235° ; from this, by aqueous potassium iodide, the *benzoyliodide*, m. p. 198°, is obtained ; the *acetyliodide*, $C_{17}H_{16}O_2N_4,CH_3\cdot COI$, has m. p. 214°. When heated at 200°, *m*-nitroanilopyrine hydrochloride loses methyl chloride, and is converted into 5-*anilino*-1-m-*nitrophenyl*-3-*methylpyrazole*, m. p. 122—123°, yellow needles.



2 : 5-endo*Anilo*-1-o-*nitrophenyl*-2 : 3-*dimethylpyrazole* (o-*nitroanilopyrine*), m. p. 111°, dark red prisms, is obtained in a similar manner to the meta-compound, using 4 mols. of aniline at 110°. It is likewise a strong base, forming a *platinichloride*, m. p. 206°, *hydriodide*, m. p. 198°, *picrate*, m. p. 167°, *thiocyanate*, m. p. 193°, *methiodide*, m. p. 97°, *ethiodide*, m. p. 177°, *propiodide*, m. p. 168°, *acetyliodide*, m. p. 225°, *benzoyliodide*, m. p. 197°, and *benzoyl chloride*, m. p. 124°; by heating the last at 50—80°/40 mm., 5-*benzoylanilino*-1-o-*nitrophenyl*-3-*methylpyrazole*, m. p. 156—157°, white prisms, is obtained. 1-*Azo*-o-*anilopyrine*, $N_2(C_6H_4\cdot C_3N_2Me_2\colon NPh)_2$, red needles, m. p. 225°, is prepared by heating an alcoholic solution of *o*-nitroanilopyrine with aluminium amalgam and a little water on the water-bath.

2 : 5-endo*Anilo*-1-p-*nitrophenyl*-2 : 3-*dimethylpyrazole* (p-*nitroanilopyrine*), m. p. 168°, dark red crystals, is prepared by heating 5-chloro-1-*p*-nitrophenyl-3-methylpyrazole with methyl sulphate and treating the resulting methosulphate with aniline at 125—130° for five hours; the *hydriodide* has m. p. 192°, and the *methiodide*, m. p. 182°. By heating the latter at 200° under reduced pressure, p-*nitro-ψ-anilopyrine*, $\begin{matrix} CMe{:}N \\ | \\ CH{:}C(NPhMe) \end{matrix}\!\!>\!N\cdot C_6H_4\cdot NO_2$, m. p. 100°, yellow needles, is obtained. p : 4-*Dinitroanilopyrine*, m. p. 192°, yellow leaflets, is prepared by heating 5-chloro-4-nitro-1-*p*-nitrophenyl-3-methylpyrazole with methyl sulphate at 115—120° for six hours, and treating the resulting methosulphate with an excess of aniline at 130° for four hours. *p*-Nitroanilopyrine yields p-*aminoanilopyrine*, m. p. 175°, by reduction with tin and hydrochloric acid, and p-*azoanilopyrine*, m. p. 224°, dark red crystals, by reduction in alcohol-chloroform solution by aluminium amalgam and water. C. S.

Action of Diethylmalonyl Chloride on Some Substances Containing Nitrogen. MARTIN FREUND and KARL FLEISCHER (*Annalen*, 1911, **379**, 27—36. Compare Abstr., 1910, i, 490).—When warmed with acetamide (2 mols.), diethylmalonyl chloride yields 4 : 6-*diketo*-2-*methyl*-5 : 5-*diethyltetrahydropyrimidine hydrochloride*,

$$C_9H_{14}O_2N_2,HCl,$$

decomp. 253°, white needles, from which dilute aqueous ammonia liberates the *base* itself, $CEt_2<\begin{matrix} CO\text{—}N \\ CO\cdot NH \end{matrix}>CMe$, m. p. 125°. The constitution follows from the ready decomposition of the base into diethylmalonamide by warm alkalis. It separates from methyl alcohol in long needles, $C_9H_{14}O_2N_2,MeOH$, m. p. 135—140°, which at 100—110° lose methyl alcohol and are converted into a vitreous, yellow mass, which has pronounced acidic properties, and is probably the enolic form of the base, since it is converted by 20% hydrochloric acid into the preceding hydrochloride. Formamide and propionamide do not form pyrimidines with diethylmalonyl chloride.

By the prolonged interaction of benzamide and diethylmalonyl chloride with warming, diethylmalonamic acid, together with a little cyaphenine, are produced. By short, careful heating, however, the two substances yield *benzoyldiethylmalonamic acid*,

$$NHBz\cdot CO\cdot CEt_2\cdot CO_2H,$$

m. p. 127—128° (decomp.), together with *diethylacetylbenzamide*, $NHBz\cdot CO\cdot CHEt_2$, m. p. 138—139°, which is also formed by heating the preceding acid above its m. p.

When warmed with diethylmalonyl chloride, benzylidenesemicarbazone is converted into 3 : 5-*diketo*-1 : 2-*diethylmalonyl*-4 : 4-*diethylpyrazolidine*, $CEt_2<\begin{matrix} CO\cdot N\cdot CO \\ | \\ CO\cdot N\cdot CO \end{matrix}>CEt_2$, m. p. 202—203°. This is converted by warm dilute sodium hydroxide and subsequent acidification into *bisdiethylmalonhydrazinic acid*, $N_2H_2(CO\cdot CEt_2\cdot CO_2H)_2$, m. p. 233—234° (decomp.), which is very stable to alkalis and to sulphuric acid, but is converted by careful heating into *bis-α-ethylbutyrylhydrazide*, $N_2H_2\cdot CO\cdot CHEt_2$, m. p. 234°.

[With MAX ROTHSCHILD.]—Benzylidenesemicarbazone and dipropylmalonyl chloride yield the corresponding 3 : 5-*diketo*-1 : 2-*dipropylmalonyl*-4 : 4-*dipropylpyrazolidine*, $C_{18}H_{28}O_4N_2$, m. p. 189°. C. S.

[Benzoylenecarbamide.] HERMANN FINGER and H. GÜNZLER (*J. pr. Chem.*, 1911, [ii], **83**, 198—199).—The substance designated as ethyl cyanoanilide-*o*-carboxylate (Finger and Zeh, Abstr., 1910, i, 382) has been described previously by Griess under the name ethoxycyanoaminobenzene (4-keto-2-ethoxy-1 : 4-dihydro-1 : 3-benzdiazine); he also mentions its conversion into benzoylenecarbamide. If this constitution is correct, the substance obtained from it by the action of methyl sulphate and described as *o*-carbethoxyphenylmethylcarbodi-imide (Finger, Abstr., 1910, i, 383) may very possibly be 4-keto-2-ethoxy-3-methyl-3 : 4-dihydro-1 : 3-benzdiazine,

$$C_6H_4<\begin{matrix}N{=}C(OEt)\\ CO\cdot NMe\end{matrix}.$$ C. S.

Condensation of Esters of Alkyloxy-acids with Cyanides and Ketones. REINHOLD VON WALTHER (*J. pr. Chem.*, 1911, [ii], **83**, 171—182).—[With H. LITTER.]—*Phenoxyacetylacetophenone*,

$$OPh\cdot CH_2\cdot CO\cdot CH_2\cdot COPh,$$

m. p. 79—80°, white needles, obtained by acidifying the product of the condensation of equimolecular quantities of ethyl phenoxyacetate and acetophenone in the presence of sodium ethoxide, gives a red coloration with alcoholic ferric chloride, does not react with phenylcarbimide or with benzoyl chloride and sodium hydroxide, but condenses with phenylhydrazine to form 1 : 3-*diphenyl*-5-*phenoxymethylpyrazole*, $OPh\cdot CH_2\cdot C<\begin{matrix}CH{-}CPh\\ NPh\cdot N\end{matrix}$, m. p. 88°, which is reduced by sodium and alcohol to 1 : 3-diphenyl-5-methylpyrazoline, phenol being eliminated. 3-*Phenyl*-5-*phenoxymethylpyrazole*, m. p. 104°, is obtained by boiling an alcoholic solution of phenoxyacetylacetophenone with aqueous hydrazine, whilst 3-*phenyl*-5-*phenoxymethyl*iso*oxazole*, m. p. 61°, is produced in a similar manner with hydroxylamine hydrochloride.

[With P. HERSCHEL.]—*a*-*Phenoxyacetylphenylacetonitrile*,

$$OPh\cdot CH_2\cdot CO\cdot CHPh\cdot CN,$$

m. p. 125—126°, prepared from ethyl phenoxyacetate, phenylacetonitrile, and sodium ethoxide, dissolves in aqueous ammonia, and reacts with phenylhydrazine in boiling glacial acetic acid to form 5-*imino*-1 : 4-*diphenyl*-3-*phenoxymethylpyrazolone*, $OPh\cdot CH_2\cdot C<\begin{matrix}N{-}{-}{-}NPh\\ CHPh\cdot C{:}NH\end{matrix}$, m. p. 120—121°, the *hydrochloride*, *platinichloride*, m. p. 192° (decomp.), *picrate*, m. p. 163°, *benzoyl* derivative, m. p. 163—169°, and *acetyl* derivative, m. p. 174—175°, of which are described. Phenoxyacetyl phenylacetonitrile reacts with dry ammonia at 150° to form *β*-*amino*-*γ*-*phenoxy*-*a*-*phenylcrotononitrile*, $OPh\cdot CH_2\cdot C(NH_2){:}CPh\cdot CN$, m. p. 88—89°, and with aniline, *p*-toluidine, and *a*-naphthylamine to form corresponding *β*-anilino-, *β*-*p*-toluidino-, and *β*-naphthylamino-derivatives, m. p. 131°, 118°, and 145—150° respectively; also, by saturating

its solution in hot glacial acetic acid with hydrogen chloride it yields *γ-phenoxy-α-phenylacetoacetamide*, $OPh\cdot CH_2\cdot CO\cdot CHPh\cdot CO\cdot NH_2$, m. p. 151—152°, which reacts with hydroxylamine hydrochloride in boiling acetic acid to form 4-*phenyl*-3-*phenoxymethyl*iso*oxazolone*,

$$OPh\cdot CH_2\cdot C{<}\begin{matrix}N\text{———}O\\ CHPh\cdot CO\end{matrix},$$

m. p. 160—162° (decomp.), and with phenylhydrazine to form 2 : 4-*diphenyl*-3-*phenoxymethylpyrazolone*, $OPh\cdot CH_2\cdot C{<}\begin{matrix}NPh\cdot NH\\ CPh\cdot CO\end{matrix}$, m. p. 145°, a substance which is soluble in sodium hydroxide, carbonate, or hydrogen carbonate. Ethyl phenoxyacetate condenses with *p*-chlorophenylacetonitrile to form *p-chloro-α-phenoxyacetylphenylacetonitrile*,

$$OPh\cdot CH_2\cdot CO\cdot CH(C_6H_4Cl)\cdot CN,$$

m. p. 168°, from which the following substances are produced by reactions similar to the preceding: 5-*imino*-1-*phenyl*-4-p-*chlorophenyl*-3-*phenoxymethylpyrazolone*, m. p. 107° (*hydrochloride*, *picrate*, m. p. 165°, *acetyl* derivative, m. p. 219°, *benzoyl* derivative, m. p. 219—220°); *β-amino-γ-phenoxy-α-*p*-chlorophenylcrotononitrile*, m. p. 132°; the corresponding *β-anilino-* and *β*-p-*toluidino*-derivatives have m. p. 122° and 135° respectively. *p*-Chloro-α-phenoxyacetylphenylacetonitrile, unlike the non-halogenated cyanide, reacts with hydroxylamine hydrochloride in boiling alcohol to form 5-*imino*-4-p-*chlorophenyl*-3-*phenoxymethyl*iso*oxazolone*, $OPh\cdot CH_2{<}\begin{matrix}CH(C_6H_4Cl)\cdot C{:}NH\\ N\text{————————}O\end{matrix}$, m. p. 108°. Also, it does not form an amide, but with alcoholic hydrogen chloride yields *ethyl γ-phenoxy-α-*p*-chlorophenylacetoacetate*,

$$OPh\cdot CH_2\cdot CO\cdot CH(C_6H_4Cl)\cdot CO_2Et,$$

m. p. 70°; the *methyl* ester has m. p. 87°. With phenylhydrazine in boiling alcohol, the ester yields a *phenylhydrazide*,

$$OPh\cdot CH_2\cdot CO\cdot CH(C_6H_4Cl)\cdot CO\cdot NH\cdot NHPh,$$

m. p. 125—126°, which is easily converted by alcoholic sodium hydroxide into the *pyrazolone*, $OPh\cdot CH_2\cdot C{<}\begin{matrix}C(C_6H_4Cl)\cdot CO\\ NPh\text{———}NH\end{matrix}$, m. p. 166°.

C. S.

Reaction Products of Potassium *iso*Cyanate and Diaminoacetone Hydrochloride. Amino- and Carbamido-propyleneureine [Carbamidomethylglyoxalone]. ANTOINE P. N. FRANCHIMONT and J. V. DUBSKY (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 13, 625—628).—It is shown that when potassium *iso*cyanate and diaminoacetone hydrochloride interact, the products are not those described by Rügheimer (Abstr., 1892, ii, 952), but 4-carbamidomethylglyoxalone and aminopropyleneureine [4-aminomethylglyoxalone] hydrochloride.

Aminomethylglyoxaline hydrochloride, $\begin{matrix}NH\cdot CH\\ CO\cdot NH\end{matrix}{>}C\cdot CH_2\cdot NH_2,HCl$, crystallises in small needles which are very soluble in water. The free base has not yet been isolated, but some of its compounds and derivatives are described. The *nitrate* and normal and acid *sulphates* all form small, colourless needles with no definite melting point. The

triacetyl derivative forms needles, m. p. 141°. The *tetra-acetyl* derivative, $\begin{matrix}NAc\cdot CH\\ | \\ CO\cdot NAc\end{matrix}\!\!>\!CH_2\cdot NAc_2$, crystallises in plates, m. p. 163—164°.

The *carboxymethyl* derivative forms leaflets, m. p. 238°, and when boiled with acetic anhydride yields a *monoacetyl* derivative,

$$C_3N_2H_3\cdot CH_2\cdot NHAc,$$

m. p. 215°. The *diacetyl* derivative crystallises in needles, m. p. 125—126°. The corresponding *carboxyethyl* derivative forms, small glittering crystals, m. p. 208°. It yields a *monoacetyl* compound, m. p. 218—219°, and a *diacetyl* compound, m. p. 101—102°.

4-*Carbamidomethylglyoxalone*, $\begin{matrix}NH\cdot CH\\ | \\ CO\cdot NH\end{matrix}\!\!>\!CH_2\cdot NH\cdot CO\cdot NH_2$, was obtained from diaminoacetone hydrochloride with 2 molecules of potassium *iso*cyanate, and also from aminomethylglyoxalone hydrochloride with 1 molecule of the *iso*cyanate. It forms snow-white leaflets, decomposing at 220°, and gives no precipitate with silver nitrate or mercuric chloride unless ammonia is added, but is precipitated by mercuric nitrate. N. C.

Phenanthrene Series. XXIX. Phenantriazines. JULIUS SCHMIDT, OTTO SCHAIRER, and ERNST GLATZ (*Ber.*, 1911, 44, 276—282. Compare Thiele and Bihan, Abstr., 1899, i, 47).—Hydroxyphenantriazine, $\begin{matrix}C_6H_4\cdot C{:}N\cdot CO\\ | \quad\quad | \quad\quad | \\ C_6H_4\cdot C{:}N\cdot NH\end{matrix}$ or $\begin{matrix}C_6H_4\cdot C{:}N\cdot C\cdot OH\\ | \quad\quad | \quad\quad \| \\ C_6H_4\cdot C{:}N\cdot N\end{matrix}$, is formed when phenanthraquinonemonoxime is boiled for ten hours with an alcoholic solution of semicarbazide hydrochloride, hydroxylamine being formed at the same time. Substituted derivatives of phenanthraquinonemonoxime react in much the same manner, and by using the 4-nitro-derivative it has been found possible to isolate the semicarbazone of the monoxime as an intermediate product. It has not been found possible to obtain the phenantriazine directly from phenanthraquinonemonosemicarbazone.

Phenanthraquinonesemicarbazone, $\begin{matrix}C_6H_4\cdot C{:}N\cdot NH\cdot CO\cdot NH_2\\ | \quad\quad | \\ C_6H_4\cdot CO\end{matrix}$, crystallises from alcohol in golden, crystalline nodules or in long, brilliant golden-yellow needles containing 0·5 mol. of ethyl alcohol. Both forms have m. p. 220° (decomp.).

3-*Hydroxyphenantriazine*, $C_{15}H_9ON_3$, crystallises from alcohol in pale yellow nodules, m. p. 285° (decomp.), and does not give the usual reactions for ketones.

4-*Nitrophenanthraquinonemonosemicarbazone*, $C_{15}H_{10}O_4N_4$, forms a yellow, crystalline powder, m. p. 210—211° (decomp.).

4-*Nitrophenanthraquinoneoximesemicarbazone*, $C_{15}H_{11}O_4N_5$, forms a yellowish-green powder, m. p. 240° (decomp.), and yields 8-*nitro-3-hydroxyphenantriazine*, $C_{15}H_8O_3N_4$, as a yellow powder, m. p. 285° (decomp.), when heated with alcohol and concentrated hydrochloric acid.

3-*Bromophenanthraquinoneoximesemicarbazone* form pale yellow, crystals, m. p. 274—275°, and 7-*bromo-3-hydroxyphenantriazine* yellow crystals, m. p. 304°.

3-*Nitrophenanthraquinoneoximesemicarbazone* has m. p. 249—250° (decomp.), and 7-*nitro-3-hydroxyphenantriazine* forms ochre-yellow crystals, m. p. 273—274° (decomp.). J. J. S.

Hypocaffeine and its Decomposition. HEINRICH BILTZ and PAUL KREBS (*Ber.*, 1911, **44**, 282—305. Compare Abstr., 1910, i, 521, 524, 526).—The products described by Fischer (Abstr., 1882, 217; 1883, 356) under the names of hypocaffeine, caffoline, and acecaffeine have been re-examined. The formula for hypocaffeine is shown to be $C_8H_{10}O_4N_4$, and not $C_6H_7O_3N_3$, as suggested by Fischer. A 60% yield of the compound is formed when trimethyluric-acid-glycol ether is decomposed by an alcoholic solution of hydrogen chloride in the absence of water; when aqueous hydrochloric acid is used, the yield is only 30%, and *apo*caffeine is also formed. The formulæ for the silver and barium salts are $C_8H_9O_4N_4Ag$ and $(C_8H_9O_4N_4)_2Ba$ respectively. When trimethyluric-acid-glycol ether is decomposed by concentrated sulphuric acid, *apo*caffeine and not hypocaffeine is formed. Caffoline has the formula $C_7H_{12}O_3N_4$, and in the conversion of hypocaffeine into caffoline by warming with barium carbonate solution a molecule of water is added and one of carbon dioxide eliminated, and the conversion of caffoline into acecaffeine by boiling with acetic anhydride and hydrolysing the resulting acetyl derivative also consists in the addition of water and the removal of carbon dioxide and ammonia. These conclusions have been confirmed by molecular-weight determinations and the methylation of hypocaffeine to oxytetramethyluric acid (Fischer, Abstr., 1898, i, 180). In the conversion of the glycol ether into hypocaffeine, trimethyluric-acid-glycol is probably first formed; this is, however, unstable, and is ruptured at the 3 : 4 position, yielding 5-hydroxy-1-methylhydantoyl-7 : 9-dimethylcarbamide,

$$\begin{array}{l}\mathrm{NHMe{\cdot}CO{\cdot}NMe{\cdot}CO{\cdot}\underset{|}{C}(OH){\cdot}NMe} \\ \qquad\qquad\qquad\qquad\quad \mathrm{CO\text{———}NH}\end{array}\!\!>\!\mathrm{CO}$$

by the hydrolytic decomposition of this in the 8 : 9 position, and (*a*) subsequent formation of a lactone, *apo*caffeine,

$$\begin{array}{l}\mathrm{NMe{\cdot}CO} \\ \mathrm{CO\text{——}O}\end{array}\!\!>\!\mathrm{C}\!<\!\!\begin{array}{l}\mathrm{NMe{\cdot}CO} \\ \mathrm{CO\text{—}NH}\end{array},$$

is formed, or (*b*) ring formation between carbon No. 5 and nitrogen No. 9, hypocaffeine, $\begin{array}{l}\mathrm{NMe{\cdot}CO} \\ \mathrm{CO{\cdot}NMe}\end{array}\!\!>\!\mathrm{C}\!<\!\!\begin{array}{l}\mathrm{NMe{\cdot}CO} \\ \mathrm{CO\text{—}NH}\end{array}$, is obtained. According to Baeyer's nomenclature (*Ber.*, 1900, **33**, 3771), hypocaffeine is thus 1 : 7 : 9-*trimethyl*-spiro-5 : 5-*hydantoin*, and oxytetramethyluric acid, the corresponding 1 : 3 : 7 : 9-tetramethyl derivative. This constitution of oxytetramethyluric acid has been confirmed by its synthesis from dimethylcarbamide and 5-hydroxy-1 : 3-dimethylhydantoylamide or 5-hydroxy-1 : 3-dimethylhydantoylmethylamide (*loc. cit.*, p. 521) (*allo*-caffuric acid), $\mathrm{CO}\!<\!\!\begin{array}{l}\mathrm{NHMe} \\ \mathrm{NHMe}\end{array} + \begin{array}{l}\mathrm{NH_2{\cdot}CO{\cdot}\underset{|}{C}(OH){\cdot}NMe} \\ \qquad\quad\;\; \mathrm{CO\text{——}NMe}\end{array}\!\!>\!\mathrm{CO} =$

$$\begin{array}{l}\mathrm{NMe{\cdot}CO} \\ \mathrm{CO{\cdot}NMe}\end{array}\!\!>\!\mathrm{C}\!<\!\!\begin{array}{l}\mathrm{NMe{\cdot}CO} \\ \mathrm{CO\text{—}NMe}\end{array} + \mathrm{NH_3 + H_2O}.$$

Hypocaffeine is not formed when methylcarbamide is fused with 5-hydroxy-1 : 3-dimethylhydantoylamide, or yet by heating dimethyl-

carbamide with caffuric acid alone or in presence of solvents, but can be synthesised together with oxytetramethyluric acid by heating dimethylcarbamide with 5-hydroxy-1-methylhydantoylmethylamide at 150° for eight to ten minutes whilst hydrogen chloride is passed through the mixture.

A *spiro*-dihydantoin is not formed by the decomposition of 7:9-dimethyluric-acid-glycol, as the rupture then occurs at the 8 : 9 position only. These facts are in perfect harmony with Biltz's views on the stability of the C·N union (*loc. cit.*, p. 324), when methyl is attached to the nitrogen. The formation of *spiro*-hydantoins is to be expected only when the uric acid is alkylated in position 3. Fischer's hypoethyltheobromine (Abstr., 1883, 357) is undoubtedly 1 : 9-*dimethyl*-7-*ethyl* spiro-5 : 5-*dihydantoin*.

Further support for the constitutional formula for hypocaffeine is afforded by an examination of the decomposition products of caffoline, namely, dimethylcarbamide or cholesterophan and methylcarbamide, from which it is argued that caffoline must be 1 : 3 : 6-*trimethylallantoin* (annexed formula), the formula of which is in harmony with most of the properties described by Fischer.

$$ {}^{2}\mathrm{CO}\!<\!\begin{array}{l}\overset{3}{\mathrm{N}}\mathrm{Me}\cdot\overset{4}{\mathrm{C}}\mathrm{O}\\ \underset{1}{\mathrm{N}}\mathrm{Me}\cdot\underset{5}{\mathrm{C}}\mathrm{H}\cdot\underset{6}{\mathrm{N}}\mathrm{Me}\cdot\underset{7}{\mathrm{C}}\mathrm{O}\cdot\underset{8}{\mathrm{N}}\mathrm{H}_2\end{array} $$

Caffoline and acetic anhydride yield acetylacecaffeine, carbon dioxide, and acetamide: $C_7H_{12}O_3N_4 + (CH_3{\cdot}CO)_2O = C_8H_{13}O_3N_3 + CO_2 + CH_3{\cdot}CO{\cdot}NH_2$, and the acetyl derivative when heated with concentrated hydrochloric acid yields acecaffeine hydrochloride, from which the free base is formed by the action of magnesium oxide and extracting the dry mass with benzene. The constitution 5-*methylamino*-1 : 3-*dimethylhydantoin*, $\mathrm{CO}\!<\!\begin{array}{l}\mathrm{NMe}\cdot\mathrm{CO}\\ \mathrm{NMe}\cdot\mathrm{CH}\cdot\mathrm{NHMe}\end{array}$, is suggested for acecaffeine, and this agrees with its basic properties, with the readiness with which it can be oxidised to cholesterophan, and with the formation of methylamine, dimethylcarbamide, and glyoxylic acid on hydrolysis.

Caffoline can be synthesised by evaporating an aqueous solution of acecaffeine hydrochloride and potassium cyanate to dryness on the water-bath.

Free acecaffeine condenses readily with alkyl carbimides or thiocarbimides, yielding alkylated allantoins and thioallantoins, and this appears to be an extremely convenient method for the preparation of these types of compounds.

It is pointed out that the oxidation of uric acid and its monomethyl derivatives cannot be due to the intermediate formation of *spiro*-hydantoins, as, according to such a scheme, both 1-methyl and 9-methyluric acids should yield 3-methylallantoin, and the 3-methyl and 7-methyl acids should yield 1-methylallantoin, whereas Fischer and Ach (Abstr., 1900, i, 63) have shown that 3-methylallantoin is formed from the 1- and 7-methylated acids, and 1-methylallantoin from the 3- and 9-methylated acids.

Hypocaffeine has m. p. 185—186° (corr.), and 1 : 3 : 6-trimethylallantoin (caffoline), m. p. 197° (corr.). Hypocaffeine can also be obtained from 5-chloro-1 : 3 : 7-trimethyl*iso*uric acid (Abstr., 1911, i, 168) and the corresponding 5-alkyloxy-compounds, but this method

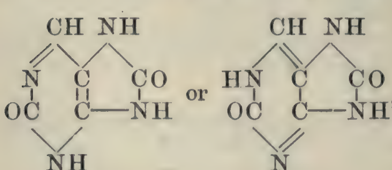
is not so convenient as Fischer's. In the alkylation of silver hypocaffeine by methyl iodide, the yield of oxytetramethyluric acid is only about 25—30%, and appreciable quantities of free hypocaffeine are formed. This is attributed to the conversion of a portion of the methyl iodide into hydrogen iodide and ethylene. When ethyl iodide is used, the silver compound is not alkylated. It has not been found possible to oxidise trimethyluric acid to a trimethylallantoin.

1 : 3 : 6 : 8-*Tetramethylallantoin*, $C_8H_{14}O_3N_4$, is readily formed when acecaffeine and methylcarbimide in benzene solution are sealed in a glass tube and left for twelve hours; it is also formed by the action of barium hydroxide solution on oxytetramethyluric acid. It absorbs water rapidly, yielding a monohydrate, which crystallises in rectangular prisms, m. p. 92°, after sintering at 85°. The anhydrous compound has m. p. 112—113°.

8-*Phenyl*-1 : 3 : 6-*trimethylallantoin*, $C_{13}H_{16}O_3N_4$, obtained from phenylcarbimide and acecaffeine in benzene solution and in the absence of moisture, crystallises from ethyl acetate, and has m. p. 197—198°. 7-*Thio*-1 : 3 : 6 : 8-*tetramethylallantoin*, $C_8H_{14}O_2N_4S$, crystallises from benzene in prisms, m. p. 158—159°. 7-*Thio*-1 : 3 : 6-*trimethyl*-8-*ethylallantoin*, $C_9H_{16}O_2N_4S$, has m. p. 135°, and is not readily desulphurised. J. J. S.

Purines. II. An Isomeride of Xanthine; 2 : 8-Dioxypurine. Carl O. Johns (*Amer. Chem. J.*, 1911, **45**, 79—87).—In an earlier paper (Abstr., 1909, i, 192) an account was given of 2 : 8-dioxy-6-methylpurine, which was prepared by the condensation of 5 : 6-diamino-2 : 4-methylpyrimidone with carbamide. 2 : 8-Dioxypurine has now been obtained in a similar manner.

2 : 8-*Dioxypurine* (annexed formulæ), obtained in a yield of 92% of the theoretical by heating a mixture of 5 : 6-diamino-2-pyrimidone (Johnson, Johns, and Heyl, Abstr., 1906, i, 771) and carbamide at 180—190°, resembles xanthine (2 : 6-dioxypurine) in many respects, and gives the murexide reaction. If carbon dioxide is passed into a solution of the substance in potassium hydroxide, or if a solution in a mineral acid is poured into water, the free base is precipitated. 2 : 8-Dioxypurine can be distinguished from xanthine by means of its *sodium* salt, which forms stout prisms containing $4H_2O$. The *hydrochloride, dinitrate*, and *ammonium* and *potassium* salts are also described; the last-mentioned crystallises with $2H_2O$.



5 : 6-Diamino-2-pyrimidone can be obtained in a yield of 65% of the theoretical by reducing 5-nitrocytosine with ferrous hydroxide; its *hydrochloride*, $C_4H_6ON_4,2HCl$, *sulphate*, $C_4H_6ON_4,H_2SO_4,H_2O$, and *nitrate*, $C_4H_6ON_4,4HNO_3$, are described. When this compound is heated with sulphuric acid of 20% strength in a sealed tube at 140—150°, it is converted into *iso*barbituric acid. E. G.

Quadriurates. RUDOLF KOHLER (*Zeitsch. physiol. Chem.*, 1911, **70**, 360—387).—Attempts were made to prepare the quadriurates first described by Bence Jones (this Journ., 1862, **15**, 201) by mixing saturated sodium biurate solution with a primary phosphate, and by introducing uric acid into hot acetate solutions of varying concentration. The salts were also sought for in snake excrement. The salts have not the composition $H_2C_5H_2O_3N_4,MHC_5H_2O_3N_4$ attributed to them by Bence Jones, but appear to be a mixture of primary urate and uric acid in the proportion of 1 : 1. By varying the concentration of the acetate solution, mixtures varying in concentration to biurate may be obtained. It is shown that this is in agreement with theoretical considerations.

The hydrolysis by water is not characteristic of the so-called quadriurates, as some do not show it at all, whereas some biurates are hydrolysed. It is due to the partial absorption of acid during the formation of the salt: this passes out into water and causes decomposition. The same reasoning applies to the decomposition of snake excrement by water, and to simultaneous precipitation of biurate and uric acid from human urine, as witnessed by the decrease in acidity after the formation of sediment. E. F. A.

Action of Azoimide on the Carbylamines. E. OLIVERI-MANDALÀ and B. ALAGNA (*Gazzetta*, 1910, **40**, ii, 441—444. Compare Abstr., 1910, i, 343).—By the action of azoimide on the corresponding carbylamines, other homologous tetrazoles can be prepared in the manner already described for 1-methyltetrazole. 1-*Ethyltetrazole*, $C_3H_6N_4$, is a liquid, b. p. 155—156°/14 mm.; it forms a stable *platinichloride*, $(C_3H_6N_4)_2PtCl_4$. 1-Phenyltetrazole (compare Freund and Paradies, Abstr., 1901, i, 770) has m. p. 65—66°. R. V. S.

The Course of the Sandmeyer Reaction. GUSTAV HELLER and WALTER TISCHNER (*Ber.*, 1911, **44**, 250—255. Compare Abstr., 1910, i, 240).—The authors have investigated the velocity of decomposition of benzenediazonium chloride, and also of *o*- and *p*-toluenediazonium chlorides, in aqueous hydrochloric acid solution in the presence of cuprous chloride by measuring the rate of evolution of nitrogen.

It is found that the velocity depends not only on the temperature and concentration both of the acid and of the diazonium compound, but also to a great extent on the nature of the diazonium compound itself, slight changes in the constitution producing considerable differences in the course of the decomposition; catalytic influences also play a considerable part in determining the rate of decomposition.

In the case of benzenediazonium chloride, free nitrous acid and also excess of cuprous chloride influence the decomposition in a marked, but irregular, manner. With *p*-toluenediazonium chloride, the velocity at the beginning of the reaction is very small, and then gradually increases; this increase is followed by a gradual diminution in the rate of decomposition, and, finally, by a rapid rise to a maximum, when the reaction quickly comes to an end.

In the case of *o*-toluenediazonium chloride, the rate of decomposition is very slow at first, then rises rapidly to a maximum in about two hours, and slowly diminishes. F. B.

o-Arylazo-compounds of Heterocyclic Phenols: 3-Methyl-4-arylazo-5-hydroxy*iso*oxazole. CARL BÜLOW and ARNULF HECKING (*Ber.*, 1911, **44**, 238—250).—Knorr and Reuter's 4-benzeneazo-5-hydroxy-3-methyl*iso*oxazole, $\left.\begin{matrix}O\cdot C(OH)\\ | \\ N{:}CMe\end{matrix}\right>C\cdot N{:}NPh$ (Abstr., 1894, i, 371; compare Schiff, Abstr., 1896, i, 83), can be readily prepared by the addition of an aqueous solution of sodium acetate and hydroxylamine hydrochloride to a boiling alcoholic solution of ethyl benzeneazoacetoacetate. It dissolves in alkalis, and is reprecipitated by carbon dioxide. The *silver* salt, $C_{10}H_8O_2N_3Ag$, when slowly heated, has m. p. 208—210° (decomp.). The sodium salt, $C_{10}H_{18}O_2N_3Na,H_2O$, was prepared by Schiff and Viciani (Abstr., 1897, i, 444), who considered it to be sodium β-oximino-α-phenylhydrazonoacetoacetate,

$$HO\cdot N{:}CMe\cdot C(N\cdot NHPh)\cdot CO_2Na.$$

The authors find, however, that this sodium salt loses one molecule of water of crystallisation when kept in a vacuum over sulphuric acid, and is readily hydrolysed with the formation 4-benzeneazo-5-hydroxy-3-methyl*iso*oxazole; when treated with hydrochloric acid, it yields the original heterocyclic phenol (compare Schiff and Viciani, *loc. cit.*).

These facts are in contradiction to the view that the solubility of 4-benzeneazo-5-hydroxy-3-methyl*iso*oxazole in alkalis is due to the rupture of the *iso*oxazole ring with the formation of salts of oximinophenylhydrazonoacetoacetic acid, and support the contention of Bülow and Haas (Abstr., 1910, i, 902) that the products obtained by the action of diazonium salts on 3-substituted *iso*oxazolones are azo-derivatives of heterocyclic phenols: $\left.\begin{matrix}O\cdot C(OH)\\ | \\ N{=\!=}CR\end{matrix}\right>C\cdot N{:}N\cdot R.$

The *iso*oxazolones themselves are also represented by the hydroxylic and not the ketonic formulæ.

When 4-benzeneazo-5-hydroxy-3-methyl*iso*oxazole is boiled with concentrated potassium hydroxide solution, 2-phenyl-4-methyl-2:1:3-triazole, $\left.\begin{matrix}CMe{:}N\\ | \\ CH{=}N\end{matrix}\right>N\cdot Ph$ (von Pechmann, Abstr., 1888, 1287), and α-methylglyoxal-α-oxime-β-phenylhydrazone are produced. The authors consider that the first stage in this reaction consists in the rupture of the *iso*oxazole ring and the formation of

$$NaO\cdot N{:}CMe\cdot C(N_2Ph){:}C(ONa)_2,$$

which then loses sodium carbonate, yielding the oxime-hydrazone.

α-Methylglyoxal-α-oxime-β-phenylhydrazone,

$$HON{:}CMe\cdot CH{:}N\cdot NHPh,$$

forms yellow crystals, m. p. 147—148°, which become yellowish-brown on keeping; it reduces silver nitrate and Fehling's solutions, and gives an intense reddish-violet coloration when its solution in concentrated sulphuric acid is treated with ferric chloride or potassium dichromate. When heated with phenylhydrazine, it is converted into

methylglyoxalosazone, NHPh·N:CMe·CH:N·NHPh (von Pechmann, Abstr., 1887, 1103).

4-p-*Nitrobenzeneazo-5-hydroxy-3-methyl*iso*oxazole*, $C_{10}H_8O_4N_4$, is prepared by the interaction of equal molecular quantities of nitric acid and 4-benzeneazo-5-hydroxy-3-methyl*iso*oxazole in concentrated sulphuric acid solution; it forms felted needles, m. p. 176—177°, dissolves in strong sulphuric acid with a greenish-yellow colour, and does not give the Bülow reaction for hydrazones.

4-*Dinitrobenzeneazo-5-hydroxy-3-methyl*iso*oxazole*, $C_{10}H_7O_6N_5$, prepared in a similar manner from two mols. of nitric acid, crystallises in yellow leaflets, m. p. 184—185°.

4-o-*Tolueneazo-5-hydroxy-3-methyl*iso*oxazole*, $C_{11}H_{11}O_2N_3$, is prepared by the gradual addition of an aqueous solution of hydroxylamine and sodium acetate to a boiling alcoholic solution of ethyl *o*-tolueneazoacetoacetate; it has m. p. 154—155°, and dissolves in alkalis with a yellow colour.

4-*p*-Tolueneazo-5-hydroxy-3-methyl*iso*oxazole, $C_{11}H_{11}O_2N_3$, obtained in a similar manner from ethyl *p*-tolueneazoacetoacetate, crystallises in yellow needles, m. p. 203°(Schiff: 202°).

4-m-*Xyleneazo-5-hydroxy-3-methyl*iso*oxazole*, $C_{12}H_{13}O_2N_3$, forms orange-yellow needles, m. p. 124—125°; its salts with alkalis are decomposed by carbon dioxide.

4-α-Naphthaleneazo-5-hydroxy-3-methyl*iso*oxazole, $C_{14}H_{11}O_2N_3$, crystallises in brick-red leaflets, m. p. 172—173° (Schiff: 168—170°), and dissolves in concentrated sulphuric acid with a deep bluish-red colour.

4-β-*Naphthaleneazo-5-hydroxy-3-methyl*iso*oxazole*, $C_{14}H_{11}O_2N_3$, forms stout, brownish-yellow needles, m. p. 201—202°; its solutions in strong sulphuric acid have a reddish-orange colour.

By the interaction of sodium acetate, hydroxylamine hydrochloride and ethyl *o*-carboxybenzeneazoacetoacetate in alcoholic solution, *ethyl α-o-carboxybenzeneazo-β-oximinoacetoacetate*,

$$HON:CMe\cdot CH(N_2\cdot C_6H_4\cdot CO_2H)\cdot CO_2Et,$$

is produced. The latter compound has m. p. 207—208°, and yields 4-o-*carboxybenzeneazo-5-hydroxy-3-methyl*iso*oxazole*, $C_{11}H_9O_4N_3$, yellow leaflets, m. p. 232°, when boiled in glacial acetic acid solution.

Ethyl nitrocarboxybenzeneazoacetoacetate, $C_{13}H_{13}O_7N_3$, obtained by nitrating ethyl carboxybenzeneazoacetoacetate, crystallises in felted, yellow needles, m. p. 188—189°; the *oxime*, $C_{13}H_{14}O_7N_4$, has m. p. 222°, and could not be converted into the corresponding *iso*oxazolone.

F. B.

The State of Aggregation of Matter. I—III. Samuel B. Schryver (*Proc. Roy. Soc.*, 1910, *B*, **83**, 96—123).—I. *Action of Salts in Heterogeneous Systems and the Nature of the Globulins.*—When formaldehyde acts on a solution of Witte's peptone, a precipitate is formed. This precipitation can, however, as Sollman has shown, be inhibited by the presence of salts. The titration of the mixture by alkali, even in the absence of precipitate formation, shows that the formaldehyde has acted on the amino-groups with the formation of methyleneimino-peptones. The inhibitory action of salts on pre-

cipitate formation can, however, be explained if the methyleneimino-peptones undergo polymerisation or condensation to form more complex molecules, and behave in the same way as methyleneasparagine behaves, according to the investigations of Schiff. If the unpolymerised or uncondensed methyleneimino-peptones are of such complexity as to form colloidal solutions, they can adsorb salt molecules from solution, which sterically inhibit their reactions with one another and prevent the formation of the insoluble complexes. A quantitative investigation of the inhibitory action of a large number of salt solutions showed that (with certain explicable exceptions), those which possessed the greatest power in this respect were the best solvents of the globulins. This suggested an explanation of the nature of these substances which are soluble in salt solution, but insoluble in water. The author gives reasons for supposing that the undissolved globulins are aggregates formed by the combination of a carboxyl group in one molecule with an amino-group in another, by means of which a salt is formed which undergoes a slight, but definite, hydrolysis in the presence of water. Owing to adsorptions of salt, the dissociated globulin molecules are sterically inhibited from reaggregation; the more readily a salt is adsorbed, the greater the solvent or (diaggregating) capacity as regards the globulin. The results indicate that owing to their adsorption capacities, chemical reactions of colloids do not follow the ordinary laws of mass action. The solvent capacity of salts for globulins can be correlated with two physical properties of their aqueous solutions, namely, their surface tensions and their viscosities; the higher the surface tension and the viscosity of a salt, the smaller its solvent capacity for the globulins. The influence of the former property can be deduced from a general study of adsorption phenomena, and of the latter by an extension of Noyes and Whitney's and of Nernst's generalisations on the rate of action in heterogeneous systems, with the assumption of the existence of a diffusion layer at the limiting surfaces. Salts also exert similar action in systems other than those containing proteins. Thus, the critical solution temperature of phenol and salt solutions is shown to be a function of the surface tension of the latter. Furthermore, the solubility of certain crystalline substances in salt solutions, especially of amphoteric substances, is shown to follow similar laws to the globulins. The surface tensions and viscosities of a series of salt solutions, together with the solubility of edestin and serum-globulin in these solutions, are tabulated.

II. *Action of Formaldehyde on Witte's Peptone.*—It is shown that the precipitate is formed from the more complex constituents of the peptones. Owing to the acidic nature of the methyleneimino-peptones, the salts of the weaker acids exert a greater inhibitory capacity on precipitate formation than would be deduced from their surface tensions and viscosities, as double decomposition can take place.

III. *The Solubility of Phenol and Certain Crystalline Substances in Salt Solutions.*—The solubilities of *dl*-leucine, *dl*-phenylalanine, caffeine, benzamide, and *p*-toluidine in the series of salt solutions employed in the investigations on the globulins are tabulated.

S. B. S.

Organic Colloids. S. J. Levites (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 4—8).—Observations are recorded in reference to the solubility and precipitability of proteins and the adsorption of tannin by gelatin.

Glutin is readily soluble in solutions of iodides and thiocyanates; casein in solutions of potassium iodide, sodium thiocyanate, potassium nitrate, and sodium phosphate. Aqueous pyridine is a good solvent for various proteins. Glutin and casein are both insoluble in water and in anhydrous pyridine, but dissolve in water-pyridine mixtures, the maximum solubility corresponding with a solvent of the composition $C_5H_5N + 2H_2O$. Glutin and Witte's peptone are readily soluble in formamide, and the solutions can be diluted with water without precipitation. The formamide and aqueous pyridine solutions of the proteins are very viscous.

In regard to the precipitation of proteins, it has been found that Witte's peptone and gelatin are precipitated by cadmium iodide in very dilute solution. Solutions of zinc and cadmium sulphates only give rise to a slight opalescence when added to Witte's peptone, and have no effect on a gelatin solution.

From experiments on the adsorption of tannin by gelatin from tannin solutions of different concentrations, it has been found that the proportion of adsorbed substance diminishes as the concentration increases. For a given solution the adsorption increases with the period of swelling of the gelatin. In presence of an electrolyte (potassium aluminium sulphate), the adsorption of tannin by gelatin is diminished, and the influence of the concentration of the tannin solution on the magnitude of the adsorption is very greatly reduced.

H. M. D.

Methylation of Gelatin. Zdenko H. Skraup and B. Böttcher (*Monatsh.*, 1910, **31**, 1035—1050).—The authors find that gelatin contains a small quantity of methyl in the form of the groups ·OMe and :NMe, and that the percentage of methyl, in both forms, increases on methylation.

When hydrolysed, the methyl derivative yields histidine and arginine in quantities amounting to 10% of those furnished by gelatin itself, traces of glutamic acid, and no lysine; leucine, alanine, glycine, pyrrolidinecarboxylic acid, and phenylalanine were also found amongst the products of hydrolysis. The hexone bases and glutamic acid are thus destroyed on methylation, whereas the leucine, alanine, etc., remain unchanged.

Comparing these results with those obtained in the case of casein (Abstr., 1909, i, 748), the authors draw the conclusion that the arrangement of the glutamic acid residue in the latter compound is different from that in gelatin.

Methylgelatin, prepared by boiling a solution of gelatin in alcoholic potassium hydroxide with methyl iodide, forms an amorphous, yellow mass, which, when powdered, is almost white; it is soluble in water, and is precipitated on the addition of ammonium sulphate. The xanthoprotein reaction is more marked than with ordinary gelatin. F. B.

The Pepsin-chymosin Question. J. F. B. VAN HASSELT (*Zeitsch. physiol. Chem.*, 1910, **70**, 171—185).—The experiments quoted bear against the view that pepsin and rennin (chymosin) are one and the same substance. It is possible to obtain preparations which exhibit only one action; anti-substances also inhibit differently the two enzymatic actions. W. D. H.

Diastase and Commercial Lecithin Preparations. HERMAN LAPIDUS (*Biochem. Zeitsch.*, 1910, **30**, 39—55).—The amount of action was determined by estimating the reducing sugars formed (calculated as maltose, for which the author has worked out tables). Wohlgemuth's iodine method was not available, owing to the action of this substance on the lecithin. The lecithin inhibits the action of ptyalin to a marked extent, but not to a relatively greater extent when small amounts of saliva are employed as compared with its inhibitory action on larger amounts of saliva. There does not appear, therefore, to be any evidence of combination between saliva and lecithin. The inhibitory influence is more marked at room temperature than at body temperature. The action of lecithin on pancreas diastase is similar, although here there is not such a marked difference between the action at room temperature and body temperature. With serum diastase, the results obtained are somewhat complicated, as the amount of diastase in the serum alters (increases) with age and diminishes after extraction with ether. The lecithin in this case diminishes the action at room temperature; at body temperature it sometimes increases and sometimes diminishes the action. Generally the action is weakly inhibitory. If, however, the serum which has been extracted with ether is employed, lecithin markedly increases the diastatic action. The above experiments were carried out with ox-serum. In human serum (from placenta) the diastatic action was weak, but was increased by addition of lecithin. Similar results were obtained with syphillitic sera, in which the diastatic action is stronger than in the normal.
S. B. S.

Hæmoglobin as a Peroxydase. GABRIEL BERTRAND and FELIX ROGOSINSKI (*Compt. rend.*, 1911, **152**, 148—151; *Bull. Soc. chim.*, 1911, [iv], **9**, 149—152. Compare Wolff and Stoecklin, Abstr., 1910, i, 802).—The peroxydase character of oxyhæmoglobin is also shared by carboxyhæmoglobin and cyanohæmoglobin; it appears, therefore, not to be due to the ability of oxyhæmoglobin to part with oxygen, but to depend on the presence of iron in the molecule. W. O. W.

Extraction of Zymase by Simple Maceration. A. VON LEBEDEFF (*Compt. rend.*, 1911, **152**, 49—51).—It is not necessary to employ Buchner's method to obtain a preparation of zymase from yeast. The solution obtained by macerating one part of dried yeast with 2·5—3 parts of water, on filtering through paper after being allowed to remain overnight, has greater activity and stability than that prepared by the usual method. W. O. W.

Organic Chemistry.

Action of Formaldehyde on Petroleum Distillates: Formation of Liquid Condensation Products. ALEXANDER M. NASTUKOFF and K. L. MALJAROFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1596—1604).—On treating the fraction of ordinary kerosene of b. p. 200—250° with its own volume of formalin and 0·75 time its volume of sulphuric acid, the authors obtained, in addition to solid condensation products, also liquid condensation products of b. p. above 250°. These products, amounting to 19% of the weight of the kerosene, have very high formolite numbers (compare Abstr., 1904, i, 801). The fraction of the liquid products b. p. 186—188°/50 mm. has the formula $C_{15}H_{28}$, the formolite number 105, $D_{21\cdot5}^{21\cdot5}$ 0·8498, and n_D^{23} 1·4703; its viscosity is 2·07 compared with that of the original kerosene fraction as unity, or, in Engler degrees, 6·57 at 21°. The reaction of formation of these liquid products is regarded as a union of the methylene group of the formaldehyde with the $-C\colon C-$ group of the original naphthene or olefine, the instability of the trimethylene ring thus formed leading to the re-formation of a double linking, thus:

$$\begin{array}{l}-CH\\ \;\;\|\\ -CH\end{array} \longrightarrow \begin{array}{l}-CH\\ \;\;|\\ -CH\end{array}\!\!>CH_2 \longrightarrow \begin{array}{l}-CMe\\ \;\;\|\\ -CH\end{array},$$

The solid condensation products mentioned above are soluble in benzene, toluene, etc., and are termed soluble formolites. T. H. P.

Methyl*iso*propylethylene [δ-Methyl-Δ^β-amylene]. A. GORSKY (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1356—1358).—By converting methyl*iso*butylcarbinol, obtained by the action of acetaldehyde on magnesium *iso*butyl chloride, into the corresponding iodide or chloride, and treating the latter with alcoholic alkali hydroxide, the author obtains an hexene, C_6H_{12}, b. p. 57—58·5°/760 mm., D_4^{20} 0·6706, n_D^{20} 1·3883. If, however, the methyl*iso*butylcarbinol is prepared by reducing mesityl oxide in aqueous ether by means of sodium, the hexene has the constants: b. p. 57—59°/740 mm., D_4^{20} 0·6703, n_D^{20} 1·3884.

This hydrocarbon, which gives *iso*butyric acid on oxidation, and is probably δ-methyl-Δ^β-amylene, is accompanied by a small proportion of another, possibly δ-methyl-Δ^α-amylene. T. H. P.

Action of Hypochlorous Acid on Ethylene Hydrocarbons. [Mlle] A. UMNOVA (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1530—1543).—The action of hypochlorous acid on βδ-dimethyl-Δ^β-amylene yields: (1) *γ-chloro-βδ-dimethyl-Δ^α-amylene*, $CH_2\colon CMe\cdot CHCl\cdot CHMe_2$, a colourless liquid, b. p. 44—45°/30 mm, D_0^0 0·9229, D_0^{20} 0·9083. The corresponding alcohol, *βδ-dimethyl-Δ^α-penten-γ-ol*,

$$CH_2\colon CMe\cdot CH(OH)\cdot CHMe_2,$$

is a viscous liquid, b. p. 77—79°/21 mm., 154—156°/ordinary pressure, D_0^0 0·8599, D_0^{20} 0·8427, giving an *acetyl* derivative, $C_9H_{16}O_2$, b. p. 169—171°. On heating with 0·5% sulphuric acid solution, the

alcohol in converted into di*iso*propyl ketone. (2) The *chlorohydrin*, $OH\cdot CMe_2\cdot CHCl\cdot CHMe_2$, which was not obtained pure, and is apparently formed as an intermediate product. These results are analogous to those obtained by Lwoff (*J. Russ. Phys. Chem. Soc.*, 1884, 16, 469), Scheschukoff (Abstr., 1884, 1276; 1885, 645), and Kondakoff (Abstr., 1886, 136), by treating various unsaturated hydrocarbons with gaseous chlorine.

γ-Chloro-$\beta\delta$-dimethyl-Δ^{α}-amylene is also obtained by the action of chlorine on $\beta\delta$-dimethyl-Δ^{β}-amylene.

The action of hypochlorous acid on $\beta\delta\delta$-trimethyl-Δ^{β}-amylene yields (1) *γ-chloro-$\beta\delta\delta$-trimethyl-Δ^{α}-amylene*, $CH_2:CMe\cdot CHCl\cdot CMe_3$, b. p. 53—54°/20 mm., D_0^0 0·9199, D_0^{20} 0·9042, n_D^{20} 1·4473. The corresponding alcohol, $CH_2:CMe\cdot CH(OH)\cdot CMe_3(?)$, b. p. 75—77°/12 mm., 173—175°/ordinary pressure, D_0^0 0·8685, D_0^{20} 0·8556, forms an *acetyl* derivative, $C_{10}H_{18}O_2$, b. p. 187—188°, 83—85/20 mm. This alcohol could not be converted into the isomeric ketone by means of dilute sulphuric acid, so that its structure is somewhat uncertain. (2) Possibly a chlorohydrin, which could not be isolated. γ-Chloro-$\beta\delta\delta$-trimethyl-Δ^{α}-amylene is also obtained by the action of chlorine on $\beta\delta\delta$-trimethyl-Δ^{β}-amylene.

δ-Iodo-β-methylpentane, $CHMeI\cdot CH_2\cdot CHMe_2$, prepared by the action of hydrogen iodide on methyl*iso*butylcarbinol, has b. p. 75—77°/60 mm., D_0^0 1·4412, D_0^{20} 1·4201.

δ-Methyl-Δ^{β}-amylene, $CHMe:CH\cdot CHMe_2$, obtained by the action of alcoholic potassium hydroxide on the preceding compound, has b. p. 58—59°, D_0^0 0·6874, D_0^{20} 0·6695.

The action of hypochlorous acid on δ-methyl-Δ^{β}-amylene yields the chlorohydrin, $OH\cdot CHMe\cdot CHCl\cdot CHMe_2$, which was not isolated in a pure state, but was converted, by distilling with potassium hydroxide, into the *oxide*, $CHMe_2\cdot CH<\overset{O}{\underset{CHMe}{|}}$, a colourless liquid, b. p. 99—100°. The corresponding *β-methylpentane-$\gamma\delta$-diol*,

$$CHMe_2\cdot CH(OH)\cdot CHMe\cdot OH,$$

has m. p. 48—49°, b. p. 194—196°. T. H. P.

Course of the Intramolecular Transformations of Alkyl Bromides and the Question of the Cause of Equilibrium in Reversible Reactions. ARTHUR MICHAEL and HANS LEUPOLD (*Annalen*, 1911, 379, 263—332. Compare Faworsky, Abstr., 1907, i, 741).—The vapour densities of *iso*butyl bromide and *tert.*-butyl bromide have been determined by Blackman's and by V. Meyer's method. The results by both methods prove that at 184° only 3% of the *iso*butyl derivative, but about 50% of the tertiary compound, is dissociated. Using the Blackman apparatus, the volume of vapour of the tertiary compound agreed with the normal vapour density during the first minute, but gradually increased during half an hour owing to slow dissociation. The authors confirm Meyer and Pond's conclusion (Abstr., 1885, 1033; compare Konowaloff, *ibid.*, 1886, 9) that the dissociation is not affected by the nature of the walls of the glass vessel or by the introduction of asbestos, sand, or powdered glass. When mercury is present, a small amount of a white solid, probably mercuric bromide, is formed in the case of the tertiary compound, but the

amount is so small that it does not affect the volume of vapour. An interesting observation was made during the determination of the vapour density of *iso*butyl bromide by Victor Meyer's method. In our experiment the stopper of the small Hofmann bottle stuck, and the bromide was not vaporised until the liquid had been some minutes in the hot tube. The result indicated appreciable dissociation, due to the partial conversion of the *iso*- into the *tert.*-butyl bromide.

Formation of the tert ary bromide cannot be detected after heating the *iso*bromide at 80° fo three hundred hours or even after boiling (b. p. 91·2—91·5°) for fifty hours. At 92—95°, however, in sealed tubes 3% is tranformed after thirty hours, and at 110° the reaction proceeds fifteen times as quickly as at 92—95°. The rate of transformation appears to depend on the diameter of the tube in which the liquid compound is heated; with narrow tubes the reaction proceeds much more slowly than with wider ones at all temperatures between 110 and 235°. The velocity does not depend on the dimensions of the gaseous phase, as stated by Eltekoff, but on the size of the liquid surface. The reacti n proceeds much less readily when all the substance is in the form of vapour; for example, when the *iso*butyl bromide is heated at 140° for fourteen hours in the form of vapour no appreciable amount of tertiary bromide is formed, whereas after one hour at the same temperature in the liquid form (diam. of tube 6 mm.) 55% of the tertiary compound is formed. The equilibrium between the *iso*- and *tert.*-bromides is reached when 74% of tertiary compound is formed, and this equilibrium holds for practically all temperatures between 140° and 262°. At the higher temperatures, even at 235°, decomposition occurs, as proved by the darkening in colour and the evolution of hydrogen bromide on opening the tubes, but the amount of this decomposition does not appear to be appreciable (1% after two hours). The conversion of *tert.*-butyl bromide into the *iso*butyl bromide proceeds extremely slowly, even after fourteen hours at 140° in the liquid condition the formation of the *iso*-compound could not be detected, whereas the *iso*bromide under similar conditions has reached the equilibrium point. The transformation of the tertiary compound begins at 184°, and even after thirty-five hours only 7% is transformed into the *iso*-compound. At 235° and 262° equilibrium is attained after ten and two hours respectively, and the equilibrium mixture has the same composition as when the *iso*bromide is heated, namely, 74% of tertiary and 26% of *iso*bromide. In this reaction the liquid surface does not appear to have any appreciable affect.

The conversion of propyl into *iso*propyl bromide has been studied, but as the temperatures required are much higher, the results are not so favourable. The reaction begins at 184°, and after one hour at 237° and 262° the amounts of *iso*propyl bromide are 17% and 20% respectively; as distinct signs of decomposition were observed, attempts were not made to determine the equilibrium point. The influence of the size of the liquid surface is observable, but not marked, and at 237° and 262° the transformation takes place more readily in the gaseous than in the liquid phase. This may be due to the partial decomposition of the propyl bromide (compare Aronstein, Abstr., 1883, 172). The

transformation of *iso*propyl into propyl bromide takes place extremely slowly whether examined in the gaseous or liquid condition.

The transformation of active amyl bromide into the tertiary compound takes place quickly at 184°, and at this temperature is influenced to an appreciable extent by the dimensions of the liquid surface, but at 237° the effect of this factor is not so marked. At 184° the velocity of transformation is much smaller with the vapour than with the liquid, whereas at 237° and 262° the reverse is true.

Transformation of inactive primary *iso*amyl bromide could not be detected at 262°, and the investigation of Wichnegradsky's secondary *iso*amyl bromide (*Annalen*, 1877, **190**, 328), which is a mixture of secondary and tertiary bromide, showed that the mixture is comparatively stable, as after ten hours at 184° only 6% of the secondary compound was transformed. Tertiary amyl bromide at 166° is fairly rapidly transformed into a mixture of secondary and primary active *iso*amyl bromides. The dimensions of the liquid surface have an appreciable effect, and equilibrium appears to be attained when 12% of secondary and 7% of primary bromide are formed.

The conclusion is drawn that dissociation does not play an important part in the transformations, as many of these begin at temperatures at which dissociation does not take place, and in many cases the transformation proceeds more slowly in the vapour phase, where dissociation is marked, than in the liquid phase, where the dissociation is less. The reactions are regarded as intramolecular changes, and an attempt is made to explain the changes by reference to Michael's entropy law, to intramolecular neutralisation, and to the relative affinities of the atoms.

It is suggested that the influence of the liquid surface may be due to the fact that in the conversion of the liquid into vapour an intermediate state is formed, which is extremely sensitive to energy changes.

One of the most interesting points established is that the velocity of transformation of the butyl bromides is not in harmony with the dynamical views of equilibrium in the case of a balanced reaction. In the case of *iso-* and *tert.*-butyl bromides, equilibrium is reached at any temperature between 140° and 265° when 74% of tertiary and 26% of *iso*-bromide is present, and hence the values of K and K' for the transformation of *iso-* into tertiary and tertiary into *iso*bromide should be in the ratio 3 : 1, whereas the ratio is much greater. It is shown that when a mixture of 74% tertiary and 26% *iso*butyl bromide is heated at 110°, 140°, or 237°, no apparent change occurs in the liquid state, but that at 237° in the state of vapour a diminution of tertiary bromide is noticed, probably due to decomposition.

It is suggested that the equilibrium is static, and not dynamic, and that it does not depend on the two velocity constants, but merely on the relative amounts of the two bromides. Such a mixture may correspond with the maximum of entropy under the conditions of the experiment.

Full details are given for the preparation of the various alkyl bromides, and methods have been worked out for estimating the amounts of the isomerides present in mixtures. *tert.*-Butyl bromide

can be estimated in the presence of the *iso*bromide by shaking for fifteen minutes with fifty times its weight of water, filtering, and estimating the hydrobromic acid in the filtrate by means of standard silver nitrate and ammonium thiocyanate. A mixture of *n*- and *iso*-propyl bromide is shaken with $N/10$-aqueous silver nitrate solution for three hours, when the whole of the *iso*-compound is decomposed together with about 2·7% of the *n*-compound. With mixtures of primary, secondary, and tertiary *iso*amyl bromides, the amount of tertiary compound can be determined by shaking with water, and then the secondary by shaking with silver nitrate solution for three hours.

J. J. S.

Boiling Points of Aqueous Solutions of *iso*Propyl Alcohol and of Trimethylcarbinol. ANTONY G. DOROSCHEWSKY and E. V. POLJANSKY (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1448—1452).—For the b. p./760 mm. of *iso*propyl alcohol and trimethylcarbinol, the authors find the respective values 82·44° and 82·55°, which are in good agreement with those obtained by Young and Fortey (Trans., 1902, **81**, 735). The boiling points of aqueous solutions containing from 0 to 100% of *iso*propyl alcohol or trimethylcarbinol were determined at 700 mm., 760 mm. and 800 mm., the results being tabulated along with the corresponding values of dt/dp.

For the aqueous solutions of these alcohols, as with those of methyl, ethyl, and propyl alcohols, the ratio of the absolute boiling points at two definite pressures is constant. Thus with *iso*propyl alcohol, the mean values of $T/760:T/700$, $T/760:T/800$, and $T/800:T/700$ are 1·0060, 0·9963, and 1·0097 respectively, the limiting values being 1·0058—1·0062, 0·9962—0·9966, and 1·0095—1·0100. For trimethylcarbinol these ratios have the values 1·0059 (1·0058—1·0060), 0·9963 (0·9962—0·9966), and 1·0095 (1·0094—1·0096) (compare Abstr., 1910, ii, 266).

T. H. P.

Oxide from Decamethyleneglycol. I. V. EGOROFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1655—1665).—Attempts to prepare the hydroxy-acid, $OH\cdot[CH_2]_9\cdot CO_2H$, from ethyl sebacate resulted in the formation of a considerable proportion of the glycol, $OH\cdot[CH_2]_{10}\cdot OH$. In order to convert this glycol into the unsaturated hydrocarbon,

$$CH_2{:}CH\cdot[CH_2]_6\cdot CH{:}CH_2,$$

(1) the corresponding dibromo-compound was treated with alcoholic potassium hydroxide solution, and (2) the glycol itself was treated with sulphuric acid. But neither reaction gave rise to the hydrocarbon, the diethyl ether of decamethylene glycol being obtained in the first case and an oxide in the second.

ακ-Dibromodecane, $CH_2Br\cdot[CH_2]_8\cdot CH_2Br$, has m. p. 27°.

The *diethyl ether* of *decamethyleneglycol*, $OEt\cdot[CH_2]_{10}\cdot OEt$, is an oily liquid, b. p. 257—260°, D_0^0 0·8500.

Decamethylene αδ-oxide, $CH_3\cdot[CH_2]_5\cdot CH{<}\begin{array}{l}CH_2\cdot CH_2\\ O\text{——}CH_2\end{array}$, obtained by the action of sulphuric acid on decamethylene glycol, has b. p. 197—199°, D_0^0 0·8694. The action of phosphorus pentachloride or pentabromide

on the oxide shows that the latter readily undergoes conversion into the unsaturated alcohol, $OH \cdot CH_2 \cdot [CH_2]_2 \cdot CH \colon CH \cdot [CH_2]_4 \cdot CH_3$. In the case of the pentachloride, this alcohol is then transformed into an unsaturated halogen derivative, but with the pentabromide the hydrogen bromide developed readily combines with the unsaturated compound, giving $\alpha\delta$-dibromodecane, $C_{10}H_{20}Br_2$, as a yellow oil. T. H. P.

New Method for the Preparation of Ketone-Alcohols. OTTO DIELS and JACOB MARTIN JOHLIN (*Ber.*, 1911, 44, 403—410).—Ketone-alcohols of the type $OH \cdot CMeR \cdot COMe$ are obtained in the form of their phenylmethylhydrazones by the interaction of magnesium alkyl halides and diacetylphenylmethylhydrazone. The reaction takes place according to the following scheme:

$$COMe \cdot CMe \colon N \cdot NMePh + RMgX + H_2O \longrightarrow CMeR(OH) \cdot CMe \colon N \cdot NMePh.$$

On boiling the phenylmethylhydrazones with water and benzaldehyde, the keto-alcohols are obtained in the free condition.

β-Methylbutan-β-ol-γ-one (trimethylketol), $OH \cdot CMe_2 \cdot COMe$, is a colourless liquid, b. p. 142°/750 mm., D^{13} 0·9595 (compare Schmidt and Austen, Abstr., 1903, i, 2); the *phenylmethylhydrazone*,

$$OH \cdot CMe_2 \cdot CMe \colon N \cdot NMePh,$$

is a yellow liquid, b. p. 144—145°/12 mm., D^{20} 1·0179.

γ-Methylpentan-γ-ol-δ-one (*dimethylethylketol*), $OH \cdot CMeEt \cdot COMe$, a colourless liquid, b. p. 154°/750 mm., D^{13} 0·9496, is purified by converting it into the *semicarbazone*, $OH \cdot CMeEt \cdot CMe \colon N \cdot NH \cdot CO \cdot NH_2$, m. p. 150°, and distilling this in steam with phthalic anhydride; the *phenylmethylhydrazone*, $OH \cdot CMeEt \cdot CMe \colon N \cdot NMePh$, is a yellow, oily liquid, b. p. 158—159°/12 mm., D^{13} 1·0146.

β-Phenylbutan-β-ol-γ-one (*phenyldimethylketol*),

$$OH \cdot CMePh \cdot COMe,$$

forms a colourless, oily liquid, b. p. 122—123°/8 mm., D^{17} 1·0801; the *phenylmethylhydrazone*, $OH \cdot CMePh \cdot CMe \colon N \cdot NMePh$, crystallises in white prisms, m. p. 68°.

Attempts to prepare ketoses of the type $OH \cdot CRR' \cdot CO \cdot CH_2 \cdot OH$, by brominating the above ketone-alcohols and replacing the bromine by the hydroxyl group, were unsuccessful.

The interaction of equal molecular quantities of ethyl oxalate, β-methylbutan-β-ol-γ-one, and sodium ethoxide leads to the formation of a compound, which the authors consider to be a *lactone* of the following structure: $O{<}{\begin{matrix} CMe_2 \cdot CO \\ CO —— CO \end{matrix}}{>}CH_2$; it crystallises in prisms, m. p. 113°, gives a dark purple coloration with ferric chloride, and, on treatment with diazomethane in ethereal solution, yields a crystalline *methyl* derivative, $O{<}{\begin{matrix} CMe_2 \cdot CO \\ CO —— CO \end{matrix}}{>}CHMe$, having m. p. 89°.

When the condensation of β-methylbutan-β-ol-γ-one and ethyl oxalate is effected by means of two molecules of sodium ethoxide, an *isomeride*, having the formula $CH_2{<}{\begin{matrix} CMe(OH) \cdot CO \\ CO ———— CO \end{matrix}}{>}CH_2$ (?), is obtained; this has m. p. 179°, and reacts with diazomethane to form a *methyl*

derivative, $CH_2<\begin{smallmatrix}CMe(OH)\cdot CO\\ CO\text{———}CO\end{smallmatrix}>CHMe$, which crystallises in slender needles, m. p. 70°, having the appearance of glass wool. F. B.

Action of Ultra-violet Light on Glycerol. HENRI BIERRY, VICTOR HENRI, and ALBERT RANC (*Compt. rend.*, 1911, **152**, 535—536. Compare Abstr., 1910, i, 652).—When exposed to ultraviolet light in the presence of air, glycerol is decomposed with production of glyceraldehyde and other unidentified substances which combine with phenylhydrazine. If the decomposition takes place in presence of an alkali, β-acrose is formed. In both cases the yields are small, but may be improved by the addition of salts of iron, cobalt, and especially uranium, which act as catalysts (compare Neuberg, Abstr., 1908, i, 915; Berthelot and Gaudechon, this vol., ii, 170).
W. O. W.

Oxidation of Unsaturated Compounds with Organic Peroxides. I. NIKOLAUS PRILESCHAEFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1387—1418).—Most of this paper has been already published (Abstr., 1910, i, 86), the new work being as follows:

Measurements of the velocity of decomposition of benzoylhydroperoxide were made in chloroform, ether, and carbon tetrachloride at 25°. In the first two of these solvents the reaction is of the first order, the values of K being 0·06507 (chloroform) and 0·06469 (ether). In carbon tetrachloride the decomposition proceeds much more rapidly.

Octylene oxide, $C_6H_{13}\cdot CH<\begin{smallmatrix}O\\ |\\ CH_2\end{smallmatrix}$, readily reacts with acetyl chloride, giving the *compound*, $C_8H_{16}O,AcCl$, b. p. 117—118°/21 mm., D_0^0 1·0066, D_{15}^{15} 0·9951. With zinc chloride, the oxide readily undergoes isomerisation, giving a compound, b. p. 172—173°, showing intense aldehydic properties and forming a semicarbazone, m. p. 67°. The glycol, $C_8H_{16}(OH)_2$, b. p. 135—136°/20 mm., formed on hydration of the oxide, is a vaselin-like mass, m. p. 45—46°, and gives a *diacetyl* derivative, b. p. 139—140°/24 mm., D_0^0 0·9874, D_{16}^{16} 0·9739.

The interaction of di*iso*butylene and benzoylhydroperoxide results in the formation of the two oxides: $CMe_3\cdot CH_2\cdot CMe<\begin{smallmatrix}O\\ |\\ CH_2\end{smallmatrix}$ and $CMe_3\cdot CH<\begin{smallmatrix}CMe_2\\ |\\ O\end{smallmatrix}$.

The glycol formed from decylene oxide, $C_8H_{17}\cdot CH<\begin{smallmatrix}CH_2\\ |\\ O\end{smallmatrix}$, forms a vaselin-like mass, and yields a *diacetyl* derivative, $C_{10}H_{20}O_2Ac_2$, b. p. 163°/22 mm., D_0^0 0·9330, D_{16}^{16} 0·9195. Under the influence of zinc chloride, the oxide undergoes isomerisation to an aldehyde, b. p. 209—210°/762 mm. or 125—126°/50 mm.

$\beta\gamma$-Dimethyl-Δ^β-butylene and benzoylhydroperoxide yield $\beta\gamma$-dimethyl-Δ^β-butylene oxide.

*Dimethyl*cyclo*hexene oxide*, $\begin{smallmatrix}CH_2\cdot CH_2\cdot CMe\\ |\qquad\qquad |\\ CH_2\cdot CH_2\cdot CMe\end{smallmatrix}>O$, prepared from dimethyl*cyclo*hexene and benzoylhydroperoxide, has b. p. 150—151°/

756·6 mm., D_0^0 0·9340, D_4^{16} 0·9201, n_D^{16} 1·44676. The corresponding *glycol*, $C_8H_{14}(OH)_2$, m. p. 92—92·5°, gives a *monoacetyl* derivative, b. p. 128—129/22 mm., D_0^0 1·0680, D_4^{16} 1·0545, n_D^{16} 1·4689.

These results show that benzoylhydroperoxide may be used as a reagent for hydrocarbons of the ethylene series, and that, under the conditions employed by the author, it allows of the estimation of the double linkings in a hydrocarbon with considerable accuracy. The character of the unsaturated complex present in the hydrocarbon is also indicated, since, under the isomerising influence of acids, oxides containing the group $\begin{matrix}-CH-\\ |\\ CH_2\end{matrix}\!\!>O$ yield aldehydes, $\cdot CH_2\cdot CHO$, whilst those containing $\begin{matrix}-CH\\ |\\ -CH\end{matrix}\!\!>O$ yield ketones, $-CH_2\cdot CO-$.

Oxidation of phenylacetylene by means of benzoylhydroperoxide yields phenylacetic acid. T. H. P.

Two-Component Systems. I. Ether–Hydrobromic Acid, Ether–Chlorine, and Ether–Bromine. DOUGLAS McINTOSH (*J. Amer. Chem. Soc.*, 1911, **33**, 71—75).—Studies of these two-component systems were made in connexion with the investigation of the compounds formed by organic substances containing oxygen with the halogens and halogen acids. The results are tabulated and plotted as curves.

On adding liquid hydrogen bromide to ether, the f. p. (−118°) is slightly depressed, and then the compound, $C_4H_{10}O,HBr$, separates; further addition raises the m. p., and at −40° the ether hydrobromide melts. On adding more of the acid, the f. p. falls until the eutectic point is reached, when a mixture of solid hydrogen bromide and a compound separates; this occurs at about −115°, and the liquid contains 12% of ether. The f. p. then rises to −86°, the m. p. of hydrogen bromide. Ethyl ether forms two compounds with hydrogen bromide, namely, $C_4H_{10}O,HBr$ (Archibald and McIntosh, Trans., 1904, **85**, 919) and $C_4H_{10}O,2HBr$, in which the oxygen may be regarded as sexavalent; the latter compound has m. p. −46°, but the f.-p. curve shows no break at this temperature.

With chlorine, ether yields the compound $C_4H_{10}OCl_2$ (Trans., 1905, **87**, 784), which melts at −51°; further addition of chlorine lowers the m. p. to −103°. Pure chlorine melts at −101·5°.

Ether unites with bromine to form the compound $C_4H_{10}OBr_2$ (*loc. cit.*). The addition of bromine depresses the f. p. of this compound, and at −119·5°, solid ether and ether dibromide separate. The dibromide melts at −38°, and, on adding more bromine, the compound $C_4H_{10}OBr_3$, m. p. 23°, is produced (Schutzenberger, *Annalen*, 1864, **129**, 50). On continuing to add bromine, the f. p. falls, and at −20° bromine and the tribromide separate. E. G.

Influence of the Medium on the Formation of Oxonium Dibromides of Simple Ethers. WLADIMIR W. TSCHELINZEFF and W. K. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1614—1630. Compare Abstr., 1909, i, 353).—The authors have studied the formation of the oxonium dibromide corresponding with ethyl ether in

benzene, light petroleum (b. p. 81—82°/746·7 mm., D_4^{20} 0·7789), chloroform, carbon tetrachloride, ethyl bromide, ethylene dibromide, bromobenzene, and carbon disulphide at 20°, at which temperature the reaction occurs practically instantaneously in absence of solvent. The reactions were followed calorimetrically, the heats of solution of ether, bromine, and the oxonium dibromide in the various solvents being determined separately.

The results show that all these solvents exert intense retarding influences on the reaction. Such influence is conditioned by the friction between the molecules of bromine and ether and the solvent, this being complicated by the different mutual actions occurring between the reacting and resultant compounds and the solvent. The formation of a new phase in the shape of a layer of the dibromide observed in four of the eight cases exerts only a very small influence on the subsequent velocity of the reaction. In the order of increasing magnitude of their retarding effects, the solvents are carbon disulphide, carbon tetrachloride, ethyl bromide, light petroleum, ethylene dibromide, chloroform, benzene, bromobenzene. T. H. P.

Uranyl Nitrate and the Nature of its Ethereal Solution. Paul Lebeau (*Compt. rend.*, 1911, **152**, 439—441. Compare Löwenstein, Abstr., 1909, ii, 736).—Uranyl nitrate appears to form at least two compounds with ethyl ether, these being deposited in crystals when an ethereal solution of the salt is dried over calcium nitrate and cooled at about −10° and −70° respectively. The dihydrate remains when the ether is removed from these compounds by a current of dry air. W. O. W.

Action of Magnesium and Aliphatic Halogen Derivatives on Ethyl Chlorocarbonate. I. Matschurevitsch (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1582—1589).—The author has studied the formation of triethylcarbinol from magnesium, ethyl chlorocarbonate and ethyl bromide (or iodide), and that of tripropylcarbinol from magnesium, ethyl chlorocarbonate, and propyl bromide. The results show that this method affords a good means of obtaining tertiary aliphatic alcohols. The following complex compounds, formed in the second phase of the reaction (compare Reformatsky, *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 1157; Houben, Abstr., 1903, i, 825), have been obtained: (1) $C_7H_{15}\cdot O\cdot MgBr$; (2) $CEt_3\cdot O\cdot MgI,Et_2O$, which was obtained crystalline; (3) when propyl bromide was employed, the complex could not be isolated in a pure state. T. H. P.

Preparation of Aluminium, Chromium, and Iron Formates. Georg Muth (D.R.-P. 228668).—The usual method of preparing aluminium, chromium, and iron formates by treating the metallic hydroxide with free formic acid is expensive, and the following alternative is recommended. The metallic hydroxides in the form of a paste are treated with an aqueous solution of aluminium fluoride (50%), the calculated quantity of sodium formate added and the

insoluble sodium aluminium fluoride separated by filtration; the solution is concentrated, and the product obtained in a pure condition:

$$Al_2F_6 + Al_2F_6 + 6H{\cdot}CO_2Na = Al_2F_6,6NaF + Al_2(CO_2H)_6$$
$$Al_2F_6 + Cr_2F_6 + 6H{\cdot}CO_2Na = Al_2F_6,6NaF + Cr_2(CO_2H)_6.$$

F. M. G. M.

Direct Esterification by Catalysis; Preparation of Benzoic Esters. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1911, 152, 358—261).—The reactions that take place when a mixture of an alcohol and acid are passed over a heated catalyst of the type MO may be represented by the equations: (1) $MO + 2R{\cdot}CO_2H = (R{\cdot}CO_2)_2M + H_2O = MO + R{\cdot}CO{\cdot}R + H_2O + CO_2$; (2) $MO + 2C_nH_{2n+1}{\cdot}OH \rightleftarrows M(O{\cdot}C_nH_{2n+1})_2 + H_2O$; (3) $M(O{\cdot}C_nH_{2n+1})_2 = MO + H_2O + C_nH_{2n}$; (4) $M(O{\cdot}C_nH_{2n+1})_2 + 2R{\cdot}CO_2H = MO + 2R{\cdot}CO_2{\cdot}C_nH_{2n+1}$.

The formation of an ester according to (4) is limited by decomposition of the unstable salt by water, whereby the alcohol is regenerated. All the possible products are formed when acetic acid and alcohol are acted on by thoria at 400°. If the acid employed, however, is one that does not readily decompose according to (1), the principal reaction is that of ester formation, (2) and (3) being negligible. Thus, methyl, ethyl, propyl, *iso*butyl, *iso*amyl, and allyl benzoates are obtained in practically theoretical yield by passing a mixture of the acid (1 mol.) and the alcohol (12 mols.) over thoria at 350°. The mixture of vapours is best obtained by allowing a solution of the acid in the alcohol to drop through a capillary tube. *iso*Propyl benzoate has also been obtained in good yield in spite of the readiness with which *iso*propyl alcohol forms propylene. *cyclo*Hexanol gave a good yield of benzoate.

Similar results have been obtained with the toluic acids, but the method is less advantageous in these cases, owing to the sparing solubility of the acids.

W. O. W.

Direct Esterification and Hydrolysis by Catalysis. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1911, 152, 494—497. Compare preceding abstract).—Titanium oxide is even more effective than thorium oxide in bringing about esterification when the vapour of an alcohol and an acid is passed over it at 280—300°. This is especially the case with acetic and propionic acids. The equilibrium limit of ester formation is very rapidly attained when the acid and alcohol are in molecular proportions. Thus, with acetic acid and *iso*butyl alcohol 69·5% of ester was formed, and with *iso*butyric acid and ethyl alcohol 71% was produced. These values are slightly higher than Menschutkin's for esterification at 155°. The process is complete with large excess of acid or alcohol.

This method cannot be applied to the preparation of formates, owing to the decomposition undergone by the acid; it has been successful, however, in the case of the acetates, propionates, butyrates, *iso*butyrates, *iso*valerates, and benzoates of methyl, ethyl, propyl, butyl, *iso*butyl, *iso*amyl, and benzyl alcohols. *Benzyl* iso*valerate* has b. p. 245°. The same syntheses can be effected by thorium oxide below 300°, but less advantageously.

Complete hydrolysis occurs when an ester is mixed with excess of water vapour and passed over titanium oxide at 280—300°.

W. O. W.

Preparation of Derivatives of ββ-Dialkylpropionic Acids. FARBENFABRIKEN VORM FRIEDR. BAYER & Co. (D.R.-P. 228667).—The preparation of some ββ-dialkylpropionamides has been previously described; it is now shown that therapeutically active amides can be obtained by the action of alkalicyanoacetic ester on halogenated dialkylcarbinols, followed by hydrolysis and subsequent elimination of carbon dioxide. Ethyl cyanoacetate (113 parts) was mixed with absolute alcohol (200 parts), and slowly treated with sodium ethoxide (23 parts Na) in the same solvent; methylpropylcarbinyl bromide (151 parts) was then added, the mixture boiled until neutral, the alcohol removed by distillation, and the oily *ethyl methylpropylcarbocyanoacetate* [*a-cyano-β-methylhexoate*],

$$C_3H_7\cdot CHMe\cdot CH(CN)\cdot CO_2Et,$$

separated by treatment with water; it has b. p. 175°/35 mm. The foregoing ester was hydrolysed with alcoholic sodium hydroxide, and the *a-cyano-β-methylhexoic acid* separated by the addition of acid; this, on prolonged warming with somewhat concentrated acid, yielded *a-methylbutylmalonamic acid*, $CHMePr\cdot CH(CO\cdot NH_2)\cdot CO_2H$, which, at a temperature of 180°, was converted, by loss of carbon dioxide, into *β-methyl-*n*-hexoamide*, $C_3H_7\cdot CHMe\cdot CH_2\cdot CO\cdot NH_2$, m. p. 99°.

F. M. G. M.

Direct Synthesis of the Glycerides. ITALO BELLUCCI and R. MANZETTI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 125—128).—The authors find that the direct synthesis of the glycerides may be effected with nearly theoretical yield by heating together equivalent quantities of glycerol and the fatty acid at a moderate temperature under reduced pressure. In these circumstances the water formed is removed, and the reaction rapidly proceeds to completion. In an instance cited, a yield of 95—98% of triolein was obtained in a few hours by heating together the theoretical quantities of oleic acid and glycerol under a pressure of 2 cm., the temperature being gradually raised from 160° to 260°, and special arrangements being made to prevent volatilisation of the reagents. The glycerides obtained in this way are pure, except for traces of glycerol and acid, which can be removed readily by washing them with water, and subsequently treating them in ethereal solution with calcium hydroxide. R. V. S.

Condensation of Halogen Compounds with Ethyl ββ-Dimethylglycidate. GEORGES DARZENS (*Compt. rend.*, 1911, 152, 443—446).—The action of organomagnesium halides on ethyl ββ-dimethylglycidate has not led to the isolation of any definite compounds. If the corresponding zinc derivatives are employed, however, esters of the type $CHMe_2\cdot CR(OH)\cdot CO_2Et$ are obtained. Thus, on warming the ester with methyl iodide in toluene solution, in presence of the zinc–copper couple, and treating the product in the usual way, an 80% yield of *ethyl a-hydroxy-aβ-dimethylbutyrate*,

$$CHMe_2\cdot CMe(OH)\cdot CO_2Et,$$

is obtained. This is a liquid with a camphoraceous odour, b. p. 76°/20 mm., 172—173° under ordinary pressure. The acid resulting from hydrolysis has m. p. 70°; Perkin (Trans., 1896, **69**, 1486) gives m. p. 75—77°, but his compound may be isomeric with the author's.

From ethyl ββ-dimethylglycidate and ethyl iodide, *ethyl α-hydroxy-β-methyl-α-ethylbutyrate* was prepared. This has b. p. 76°/16 mm., 180—181° under ordinary pressure; the corresponding *acid* has m. p. 76°, b. p. 140°/22 mm. Allyl bromide gave *ethyl α-hydroxy-β-methyl-α-allylbutyrate,* b. p. 90°/21 mm., 198—199° under ordinary pressure; the corresponding *acid* has m. p. 57°, b. p. 147°/21 mm.

The molecular transformation involved in the formation of these substances may be explained by supposing that the glycidic ester first undergoes change into a pyruvic ester, which then acts normally with the zinc compound. Ethyl dimethylpyruvate was detected amongst the products of the reaction. W. O. W.

Action of the Chlorides of α-Alkyloxy-acids on Mixed Organo-metallic Zinc Compounds. EDMOND É. BLAISE and L. PICARD (*Compt. rend.*, 1911, **152**, 446—447. Compare this vol., i, 175).—A discussion of the action of organo-zinc halides on higher homologues of the acid chlorides dealt with in a previous communication.

α-Ethoxyhexoic acid on treatment with thionyl chloride furnishes *α-ethoxyhexoyl chloride,* b. p. 69°/9 mm.; *γ-ethoxyheptane,* b. p. 151°/750 mm., results when this is acted on by zinc ethyl iodide. Esters of α-alkyloxy-αα-dialkyl acids are best prepared by treating ethyl oxalate with phosphorus pentachloride, and allowing a zinc alkyl halide to act on the product. The reaction proceeds in accordance with the equation: $OEt \cdot CCl_2 \cdot CO_2Et + 2ZnRI = ZnI_2 + ZnCl_2 + OEt \cdot CR_2 \cdot CO_2Et$. The ester is contaminated with ethyl oxalate, which may be removed by shaking with ammonia. *α-Ethoxy*iso*butyric acid,* $OEt \cdot CMe_2 \cdot CO_2H$, b. p. 99°/14 mm., was prepared in 84% yield by this process. *α-Ethoxy-α-ethylbutyric acid* has b. p. 120·5°/13 mm. It was not possible to prepare the chlorides of these acids by the action of thionyl chloride, this reagent leading to profound decomposition. W. O. W.

Synthesis of β-Hydroxy-α-ethylbutyric Acid. I. MATSCHUREVITSCH (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1576—1582).—β-Hydroxy-α-ethylbutyric acid, previously prepared by Waldschmidt (Abstr., 1878, 136) and by Marshall and Perkin (Trans., 1891, **59**, 870), may be obtained by Reformatsky's method by the interaction of acetaldehyde, ethyl α-bromobutyrate, and zinc. Obtained in this way, the acid has the properties given by Waldschmidt, except that the silver salt is found to be unstable and readily soluble in water. On distillation, the acid is converted into α-ethylcrotonic acid. T. H. P.

Interchange of Alkyl Groups in Acid Esters. TELEMACHOS KOMNENOS (*Monatsh.*, 1911, **32**, 77—88. Compare Abstr., 1910, i, 361, 708).—An extension of the previous investigations. Succinic acid and methyl hydrogen succinate are produced when ethyl succinate is added to a warm solution of sodium methoxide in methyl alcohol. The hydrolysis and subsequent partial esterification are unexpected,

since the prolonged heating of ethyl succinate with alcoholic sodium ethoxide does not cause hydrolysis, but the formation of ethyl succinylsuccinate. Consequently ethyl succinate has been heated on the water-bath for forty hours with methyl-alcoholic sodium methoxide, but here, again, hydrolysis occurs, the chief product being sodium succinate; a small amount of a substance, m. p. 155°, probably methyl succinylsuccinate, is formed. When ethyl phenylacetate is heated for two hours on the water-bath with methyl-alcoholic sodium methoxide, methyl phenylacetate, b. p. 215°, D^{15} 1·050, is obtained, together with a little phenylacetic acid. Under similar conditions ethyl benzoate is partly hydrolysed and partly converted into methyl benzoate. This last example is important, in that it shows that the interchange of alkyl groups occurs in the esters of acids which do not contain an active methylene group. C. S.

Theoretical Consideration of the Isomerism of Fumaric and Maleic Acids. BORIS GLASMANN (*Pharm. Zentr.-h.*, 1911, 52, 275—281).—The author suggests that the hypothetical ortho-dicarboxylic acid, $C(OH)_3\cdot CH\!:\!CH\cdot C(OH)_3$, may lose the elements of water in different ways, whereby maleic acid, $O\!<\!\begin{array}{l}CO\text{——}CH\\ C(OH)_2\cdot \overset{\|}{C}H\end{array}$, and fumaric acid, $O\!<\!\begin{array}{l}C(OH)\cdot CH\\ \quad >O \quad \|\\ C(OH)\cdot CH\end{array}$, are produced. It is shown that the preceding constitutions serve to account for the chemical behaviour of the two acids, the conversion of the one into the other, and their formation by the oxidation of furan derivatives; also an attempt is made to explain the formation of racemic acid and of mesotartaric acid by the oxidation by potassium permanganate of fumaric acid and maleic acid respectively.

It is remarked that, in addition to maleic and fumaric acids, yet a third acid, having the constitution $CO_2H\cdot CH\!:\!CH\cdot CO_2H$, may be derived from the hypothetical ortho-dicarboxylic acid; for example, the constitutions $O\!<\!\begin{array}{l}CO\text{——}CH\\ \qquad\quad \|\\ C(OH)_2\cdot CMe\end{array}$, $O\!<\!\begin{array}{l}C(OH)\cdot CH\\ \quad >O \quad \|\\ C(OH)\cdot CMe\end{array}$, and $CO_2H\cdot CH\!:\!CMe\cdot CO_2H$ are proposed for citraconic, mesaconic, and itaconic acids respectively. C. S.

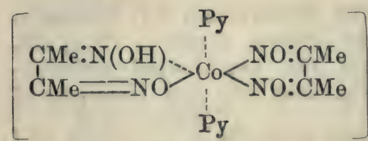
Chloral Chloroacetate. EMILIO GABUTTI (*Gazzetta*, 1911, 41, i, 111—112).—In the description of this compound previously published (Abstr., 1900, i, 370), the boiling point (224°/760 mm.) of the pure substance was omitted by a printer's error. A direct comparison of the products respectively obtained by the method formerly given and by that of Wegscheider and Späth (Abstr., 1910, i, 155) has demonstrated their identity. R. V. S.

Investigations on Complex Compounds. VII. Complexes of the Dioxime Series. LEO A. TSCHUGAEFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 1466—1487).—[With A. POSTNIKOFF.]—Further

investigations have been made on the diammino-base, $[Co2PyD_2H_2]OH$ (where $Py = C_5NH_5$), corresponding with dimethylglyoxime, which separates in the form of sparingly soluble, cinnamon-red crystals when the salts, $[Co2PyD_2H_2]X$, are treated with alkali hydroxide or ammonia. This base loses water, forming the anhydride,

$$[Co2PyD_2H],$$

on precipitation. The fact that its molecular conductivity is only $\mu = 7 \cdot 0$ for a dilution of 1000 litres confirms the co-ordination formula ascribed to it. On solution in acids, it again yields salts of the type $[Co2PyD_2H_2]X$. These transformations recall those occurring in the magenta series and with other colouring matters of similar constitution, and it may be that the loss of water is preceded by the migration of the hydroxyl group of the base from the external sphere to the cobalt atom of the inner sphere, thus creating the conditions for the loss of water and the formation of the anhydrous base. The latter probably has the annexed structure.



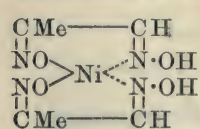
In accordance with this structure, the free base conducts the electric current only to a slight extent; the conductivity increases very considerably with the dilution, but this is probably due to hydration of the anhydrous base. Aqueous solutions of the base exhibit a distinct alkaline reaction.

[With I. Kiréeff.]—The chloride and iodide of cobaltidihydroxylaminodimethylglyoxime were prepared. The *chloride*,

$$[Co2NH_2 \cdot OHD_2H_2]Cl,$$

forms large, yellowish-brown crystals, readily soluble in water. The *iodide*, $[Co2NH_2 \cdot OHD_2H_2]I$, forms dark yellowish-brown crystals, and, on dissociation, yields two ions. These salts may be kept for a long time, and even recrystallised without appreciable alteration.

[With Iv. Tischtschenko.]—The compound formed by nickel with the dioxime of methylglyoxal exists in a dark red, unstable form and a more stable orange one. These are possibly stereoisomerides, in which the methyl groups of the dioxime occupy either the annexed *syn*-position or the *anti*-position.



Cobaltiamminochloromethylglyoximine,

$$[CoNH_3ClD_2H_2],$$

obtained by the action of methylglyoxime on purpureocobalt chloride, forms a cinnamon-red, crystalline precipitate stable towards acids.

Cobaltidiamminomethylglyoximine chloride, $[Co2NH_3D_2H_2]Cl$, obtained by the action of excess of ammonia on the preceding compound, forms dark cinnamon-red plates. The corresponding *iodide* forms dark yellowish-brown crystals; the ease with which this compound is formed from the chloride by the action of potassium iodide indicates that the iodine is present in an ionisable condition, and this is confirmed by measurements of the electrical conductivity of the salt. The free *base*, $[Co2NH_3D_2H_2]OH$, forms a dark brown solution exhibiting distinct alkaline properties.

[With B. P. Afanaséeff.]—Investigation of the decomposition of

the nickel compounds of glyoxime, methylglyoxime, dimethylglyoxime, and methylethylglyoxime by hydrochloric, hydrobromic, nitric, and acetic acids shows that the stability of these compounds increases with the complexity of the substituent groups of the glyoxime.

T. H. P.

Photochemical Synthesis of Carbohydrates from Carbon Dioxide and Hydrogen in Absence of Chlorophyll. WALTHER LÖB (*Biochem. Zeitsch.*, 1911, 31, 358—360).—A criticism of the recent work of Stoklasa and Zdobnický (this vol., i, 178). S. B. S.

Investigations of the Phosphorus Compounds of Seeds, Particularly Phytin. WŁAD. VORBRODT (*Bull. Acad. Sci. Cracow*, 1910, *A*, 414—511).—The author obtains from maize meal a solution which contains phytic acid; on evaporation, a yellow, viscous mass is left. When the solution is neutralised with barium hydroxide solution, an acid barium phytate crystallises out; this salt is white when dried in a stream of dry air, but yellow if dried more slowly. On analysis it was found that, for 6 atoms of carbon, only 5·5 of phosphorus were present, hence Posternak's formula is incorrect. Neutralisation of the acid with sodium or barium hydroxides in presence of various indicators showed that more than four hydroxyl groups occurred in the molecule, since more than four salts appeared to be formed.

On heating with water to 155°, phytic acid decomposes with formation of phosphoric acid and inositol.

Evidence was obtained of the presence of enzymes in the seed capable of splitting off phosphoric acid from the organic phosphorus compounds. E. J. R.

Contardi's Polyphosphoric Esters of Mannitol, Quercitol, Inositol, and Dextrose. PAUL CARRÉ (*Bull. Soc. chim.*, 1911, [iv], 9, 195—199. Compare Abstr., 1905, i, 814, and Contardi, Abstr., 1910, i, 157, 609).—The author has repeated Contardi's experiments, and finds that his supposed polyphosphoric esters of mannitol, quercitol, inositol, and dextrose are in reality mixtures of phosphoric acid, barium dihydrogen phosphate, and the parent substances, or their decomposition products. T. A. H.

Digestive Ferments for Manninotriose and its Derivatives. HENRI BIERRY (*Compt. rend.*, 1911, 152, 465—467. Compare Tanret, Abstr., 1902, i, 661; 1903, i, 606).—The gastro-intestinal juice of *Helix* readily hydrolyses stachyose, or manninotriose, one of the products of the partial hydrolysis of the sugar. In the latter case the final products are galactose (2 mols.) and dextrose (1 mol.), but an intermediate biose (dextrose-galactose) appears to be produced. The biose has not been isolated; it cannot be lactose, since lactase is without action on it.

The osazone of the trisaccharide undergoes hydrolysis in the same way. This compound has m. p. 122—124°, and not 192—194°, as stated by Neuberg and Lachmann (Abstr., 1910, i, 225): Tanret

gives 122°. *Manninotriosecarbamide*, $C_{18}H_{32}O_{15}:N\cdot CO\cdot NH_2,H_2O$, $[\alpha]_D^{15}$ +127·4°, is also hydrolysed by the above ferment, with formation of galactose. W. O. W.

Chemical Processes Occurring in the Preparation of Cellulose by the Sulphate Method. PETER KLASON and BROR SEGERFELT (*Arkiv. Kem. Min. Geol.*, 1911, 4, No. 6, 1—20).—The so-called sulphate method for the preparation of cellulose from wood consists in treatment of the latter with a lye containing chiefly sodium hydroxide and sodium sulphide. The chemical reactions taking place consist, for the most part, in the transformation of the gum-like carbohydrates into saccharinic acids, the latter neutralising the alkali. At the same time the lignin molecules are broken down into simpler ones, which also dissolve in the alkali because they contain hydroxyl groups; about one-fifth of the methoxy-groups in the lignin are also destroyed by saponification, thus increasing the amount soluble in the alkali.

The process of saponification in the boiling solutions give rise also to methyl alcohol, methyl mercaptan, and methyl sulphide, the methyl alcohol being formed in the greater quantity. With insufficient quantity of alkali, the quantity of methyl mercaptan increases; increasing quantity of alkali favours the formation of methyl sulphide. Under the same conditions, fir wood gives about twice as much methyl mercaptan as pine wood. Wheat straw contains fewer methoxy-groups than the woods, and gives less methyl mercaptan.

Both meta- and para-saccharinic acids are found in the liquors, together with a new form of *iso*saccharinic acid, to which the authors give the same sapin-*iso*saccharinic acid (sapin = fir); this latter acid constitutes the greater part of the saccharinic acids. Assuming that Nef's theory of the formation of the saccharinic acids is correct (Abstr., 1908, i, 5; 1910, i, 711), this points to the chief constituent of the gum-like carbohydrates in pine wood, being one of the following ketohexoses: *l*-fructose, *l*-pseudofructose, *l*-tagatose, or *d*-sorbose.

When the process of extraction is complete, about half of the hydrogen sulphide originally present in the lye is chemically combined with the lignin in the black liquors. Because of this, and because of the formation of volatile methyl-sulphur compounds, the sodium sulphide present in the lye is only gradually changed into the active sodium hydroxide. This explains the protecting action of alkali sulphide on the cellulose fibres. T. S. P.

The Nitrogenous Products of Alkaline Hydrolysis of Cellulose Nitrate. ERNST BERL and ANDOR FODOR (*Zeitsch. Schiess. Sprengstoffwesen*, 1910, 5, 254—256, 269—273).—A discussion of the results obtained by various workers on cellulose during the past ten years. It is shown that by the alkaline hydrolysis and reduction of collodion and cellulose nitrate, aliphatic nitrogenous acids are produced, their decomposition products being demonstrable as hydrogen cyanide, hydroxylamine, ammonia, and nitrous acid.

The formation of a polysaccharide by the condensation of n molecules of a hexose is stated to take place according to the formula

$nC_6H_{12}O_6 - (n-1)H_2O$ (compare Kiliani, Abstr., 1908, i, 320), and the expression $(C_6H_{10}O_5)n$ as representing the cellulose molecule is to be considered erroneous. The action of an excess of sodium carbonate on an alcohol-ether solution of collodion wool yielded after two weeks' shaking together, a colourless nitrogenous compound soluble in alkalis with a yellow coloration; after a further period of several weeks two other gelatinous, dextrin-like substances were obtained.

The action of sodium ethoxide on a highly nitrated cellulose in acetone solution resulted in denitration, yielding the hygroscopic, brown sodium salt of a nitrogenous acid, which separated on acidification as an amorphous, flocculent mass.

Cellonic acid nitrate, $C_{24}H_{33}O_{16}(NO_3)_5$, was obtained as a colourless powder by the action of alcoholic potassium hydroxide (1·8 equivalents to each nitric acid residue) on collodion wool, and its formation from glucosidohexonic acid, $C_{24}H_{38}O_{21}$, was probably preceded by the removal of $5H_2O$ (3 by anhydridisation and 2 by lactonisation) from 2 mols. of hexonic acid; it decomposes at 163°; the *phenylhydrazone*, $C_{24}H_{33}O_{13}(NO_3)_5(C_6H_5N_2H)_3$, a brown, amorphous substance, and the p-*bromophenylhydrazone*, $C_{24}H_{33}O_{13}(NO_3)_5(C_6H_4Br\cdot N_2H)_3$, a brick-red powder, were also prepared. A molecular mixture of glucosidohexonolactone trinitrite and glucosidodihexonolactone trinitrite was isolated from the alcoholic mother liquors in the form of an orange-yellow, crystalline powder.

The hydrolysis of cellulose nitrate with ammonium sulphide in absolute alcohol yielded a voluminous precipitate, which after elimination of free sulphur was found to consist of hexonolactone (90%) and hydroxypyruvic acid (10%). F. M. G. M.

The Nitrogen-free Products from the Alkaline Hydrolysis of Cellulose Nitrate. ERNST BERL and ANDOR FODOR (*Zeitsch. ges. Schiess. und Sprengstoffwesen*, 1910, 5, 296—297, 313—316. Compare *J. Soc. Chem. Ind.*, 1908, 27, 534; Abstr., 1908, i, 504, 505).—A detailed account of experiments on the detection and isolation of the nitrogen-free decomposition products obtained by the alkaline hydrolysis of cellulose nitrate. The relative proportions of the different acids formed were observed to vary according to the concentration of the alkali employed, a dilute solution yielding compounds containing 4—5 carbon atoms, whilst with concentrated alkali, acids with 1—3 carbon atoms predominated. The products detected were hydroxypyruvic acid, which was probably accompanied in the solution by its aldehydo-form, $CHO\cdot CH(OH)\cdot CO_2H$, and the keto-form,

$$CH_2(OH)\cdot CO\cdot CO_2H,$$

with malic, trihydroxyglutaric, malonic, tartronic, oxalic, glycollic, and dihydroxybutyric acids as secondary oxidation products.

The p-*nitrophenylosazone*, $C_{15}H_{12}O_6N_6$, a red, crystalline powder, m. p. 260°, and an *osazone*, m. p. 213—215°, were also prepared.

F. M. G. M.

Iso- and Hetero-poly-acids. III. The Basicity of Some Hetero-poly-acids. ARTHUR ROSENHEIM and JACOB PINSKER (*Zeitsch. anorg. Chem.*, 1911, 70, 73—85. Compare this vol., i, 109; ii, 116).—The extension of Werner's co-ordination theory to poly-acids

by Miolati and Pizzighelli (Abstr., 1908, ii, 595) facilitates the correct formulation of these acids. Many hetero-poly-acids have 12 acid anhydride molecules associated with the acid containing the central atom. As it is probable that the dimolybdate and ditungstate radicles, $(Mo_2O_7)''$ and $(W_2O_7)''$, are often present, the formulæ of some "limiting" hetero-poly-acids and salts may be written:

$H_5[IO_6]$	$H_7[PO_6]$	$H_8[SiO_6]$
$X_5[I(MoO_4)_6]$	$X_7[P(Mo_2O_7)_6]$	$X_8[Si(Mo_2O_7)_6]$
$X_5[I(WO_4)_6]$	$X_7[P(W_2O_7)_6]$	$X_8[Si(W_2O_7)_6]$.

Actually, molybdo-periodic acid and tungsto-periodic acid are known to be tribasic, and the corresponding hetero-silicic acids octobasic, but only salts of tribasic 12-molybdo- and 12-tungsto-phosphoric acids have hitherto been obtained.

It is now found that these, and the corresponding hetero-arsenic acid, yield heptabasic salts, which are proved by conductivity measurements to be normal, whilst the tribasic salts are acid.

The acid, $H_3PO_4(MoO_3)_{12},30H_2O$, is prepared by extracting an acidified solution of its salts with ether. A solution in water is then gradually mixed with a 10% solution of guanidinium carbonate, when a deep yellow, microcrystalline precipitate is formed, but dissolves on further addition of the carbonate to the warm solution. Crystals of the *heptabasic* salt, $(CH_5N_3)_7H_7[P(Mo_2O_7)_6],8H_2O$, separate on cooling, and have a greenish-yellow colour. The tribasic salt is prepared more conveniently by dissolving 12 mols. of molybdenum trioxide in a boiling solution of guanidinium carbonate (12 mols.), adding 1 mol. of phosphoric acid, and acidifying strongly with hydrochloric acid. This salt has then the composition $(CH_5N_3)_3H_7[P(Mo_2O_7)_6],10H_2O$. The conductivity of the sodium salt (which is more soluble in water) indicates the presence of acid hydrogen, whilst the conductivity of the heptabasic salt is that of a normal salt.

Two tribasic salts of an arsenomolybdic acid containing 12 mols. of molybdenum trioxide are known, but the new heptabasic *salt* contains only 10 mols. It is prepared similarly to the phosphate, and has the composition $(CH_5N_3)_7H_7\left[As\genfrac{}{}{0pt}{}{(Mo_2O_7)_5}{O}\right],5H_2O$, but decomposes when recrystallised. The conductivity corresponds with its formulation as a normal salt.

It has not been found possible to obtain an octobasic molybdosilicate. The *guanidinium* salt has the composition

$$(CH_5N_3)_4H_8[Si(Mo_2O_7)_6],6H_2O,$$

and crystallises in deep yellow leaflets. When warmed with guanidinium carbonate, silica separates, and the filtrate deposits felted needles of *guanidinium molybdate*, $(CH_5N_3)_2H_2Mo_3O_{10},5H_2O$.

C. H. D.

The Compounds of Hydrated Metallic Salts with Hexamethylenetetramine. (Labile Hydrated Forms Fixed by means of an Organic Base.) II. GIUSEPPE A. BARBIERI and F. CALZOLARI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 119—125. Compare this vol., i, 184).—Compounds of other metallic salts have now been prepared by the method adopted in the case of the halides previously described.

Magnesium thiocyanate yields a compound,

$$Mg(SCN)_2,10H_2O,2C_6H_{12}N_4,$$

whilst the thiocyanates of manganese, iron, cobalt, and nickel give compounds of the type $M''(SCN)_2,4H_2O,2C_6H_{12}N_4$. The magnesium and manganese compounds can be recrystallised from water unchanged, but the others lose a molecule of hexamethylenetetramine, forming substances of the type $M''(SCN)_2,4H_2O,C_6H_{12}N_4$, which are isomorphous.

The nitrates of magnesium, manganese, cobalt, and nickel form isomorphous compounds of the general formula

$$M''(NO_3)_2,10H_2O,2C_6H_{12}N_4.$$

The perchlorates of the same metals form compounds of the type $M''(ClO_4)_2,8H_2O,2C_6H_{12}N_4$, which are isomorphous, and can be recrystallised from water.

The *compound*, $Mg(SCN)_2,10H_2O,2C_6H_{12}N_4$, forms thin, colourless tablets, which show holosymmetry of the triclinic system [$a:b:c=0·9342:1:0·9223$; $\alpha=134°12'$, $\beta=47°4'$, $\gamma=120°56'$]. The *compound*, $Mn(SCN)_2,4H_2O,2C_6H_{12}N_4$, crystallises in colourless tablets, which exhibit holosymmetry of the tetragonal system [$a:c=1:1·0366$]. The *compound*, $Fe(SCN)_2,4H_2O,2C_6H_{12}N_4$, crystallises in colourless scales, which on recrystallisation yield the *compound*,

$$Fe(SCN)_2,4H_2O,C_6H_{12}N_4,$$

in canary-yellow crystals, which exhibit holosymmetry of the triclinic system [$a:b:c=1·4012:1:1·5723$; $\alpha=124°57'$, $\beta=29°54'$, $\gamma=121°36'$]. The *compound*, $Co(SCN)_2,4H_2O,2C_6H_{12}N_4$, forms lustrous, rose-coloured scales. On recrystallisation it yields the *compound*, $Co(SCN)_2,4H_2O,C_6H_{12}N_4$, in dark red, tabular crystals, which show holosymmetry of the triclinic system [$a:b:c=1·4232:1:1·6034$; $\alpha=128°23'$, $\beta=31°6'$, $\gamma=123°33'$]. The *compound*,

$$Ni(SCN)_2,4H_2O,2C_6H_{12}N_4,$$

is a green, crystalline powder. When recrystallised, it gives the *compound*, $Ni(SCN)_2,4H_2O,C_6H_{12}N_4$, in emerald-green, tabular crystals, which show holosymmetry of the triclinic system, and forms mixed crystals with the corresponding cobalt compound in all proportions.

The *compound*, $Mg(NO_3)_2,10H_2O,2C_6H_{12}N_4$, forms colourless, tabular crystals, which exhibit holosymmetry of the rhombic system [$a:b:c=0·8261:1:0·4813$]. The *compound*, $Mn(NO_3)_2,10H_2O,2C_6H_{12}N_4$, crystallises similarly, showing holosymmetry of the trimetric system [$a:b:c=0·8388:1:0·4894$. The *compound*, $Co(NO_3)_2,10H_2O,2C_6H_{12}N_4$, crystallises in rose-coloured scales, and forms solid solutions with the two preceding substances in all proportions. The *compound*,

$$Ni(NO_3)_2,10H_2O,2C_6H_{12}N_4,$$

forms emerald-green scales, and gives solid solutions in all proportions with the three preceding compounds.

The *compound*, $Mg(ClO_4)_2,8H_2O,2C_6H_{12}N_4$, crystallises in small, colourless, lustrous needles. The *compound*, $Mn(ClO_4)_2,8H_2O,2C_6H_{12}N_4$, crystallises similarly. The *compound*, $Co(ClO_4)_2,8H_2O,2C_6H_{12}N_4$, forms rose-coloured needles, and yields solid solutions with the analogous manganese and magnesium compounds.

The *compound*, $Ni(ClO_4),8H_2O,2C_6H_{12}N_4$, crystallises in green needles.

The crystallographic measurements were effected by E. Billows.

R. V. S.

Hydrated Additive Products of Metallic Dichromates. (Labile Hydrated Forms Fixed by means of an Organic Base.) III. GIUSEPPE A. BARBIERI and F. LANZONI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 161—164. Compare Barbieri and Calzolari, this vol., i, 184; also Parravano and Pasta, Abstr., 1907, i, 961).—Hexamethylenetetramine *compounds* of *magnesium*, *zinc*, *manganese*, *cobalt*, and *nickel dichromates* are readily obtained by acting on a concentrated solution of the acetates or sulphates of those metals with a concentrated solution of hexamethylenetetramine in the presence of potassium dichromate. For the most part they crystallise in lustrous scales, but may also be obtained in prisms. They are not very stable; even in the dark the base reduces the chromic acid, and in bright light the orange-red crystals become green superficially in a few minutes. Analysis shows that all the compounds have the composition: $M''Cr_2O_7,7H_2O,2C_6H_{12}N_4$, where M'' represents Mg, Zn, Mn, Co, or Ni, so that there is complete analogy to the mercuric cyanide compounds of Krüss and Unger (Abstr., 1895, ii, 355). R. V. S.

Compounds of Salts of [Metals of] the Rare Earths with Hexamethylenetetramine. GIUSEPPE A. BARBIERI and F. CALZOLARI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 164—169).—By the action of very concentrated solutions of hexamethylenetetramine on concentrated aqueous solutions of *cerium*, *lanthanum*, and *neodymium chlorides*, *compounds* of the type $M'''Cl_3,14H_2O,2C_6H_{12}N_4$ were obtained, whilst the *nitrates* of the same elements yielded substances of the type $M'''(NO_3)_3,8H_2O,2C_6H_{12}N_4$. *Yttrium* and *erbium chlorides* gave compounds of the form $M'''Cl_3,11H_2O,2C_6H_{12}N_4$, and the *nitrates* of these metals yielded products of the composition $M'''(NO_3)_3,10H_2O,2C_6H_{12}N_4$. All these compounds are crystalline, and are more hydrated than the corresponding simple salts of the same metals.

Crystallographic data are given in some cases (by E. Billows). The compound $NdCl_3,14H_2O,2C_6H_{12}N_4$ forms lilac-coloured, silky needles belonging to the triclinic system.

The compound $Nd(NO_3)_3,8H_2O,2C_6H_{12}N_4$ forms minute, lilac-coloured crystals, which show holosymmetry of the monoclinic system [$a:b:c = 0·7336:1:0·4329$; $\beta = 57°29·5'$].

The compound $Er(NO_3)_3,10H_2O,2C_6H_{12}N_4$, like the other erbium and yttrium compounds described, is more exactly represented by a formula, $(Er,Y)(NO_3)_3,10H_2O,2C_6H_{12}N_4$, (Er,Y), having apparent atomic weight 140; it forms pale red crystals, which show holosymmetry of the monoclinic system [$a:b:c = 1·1501:1:1·4892$; $\beta = 57°$]. R. V. S.

Combination of Amines with Acetylenic Ketones. Preparation of Ethylenic β-Substituted Amino-ketones. ÉMILE ANDRÉ (*Compt. rend.*, 1911, 152, 525—527).—The neighbourhood of a CN or CO_2R group to a triple linking confers on the compound the property of combining additively with primary and secondary amines (Moureu and Lazennec, Abstr., 1906, i, 956). The carbonyl group is effective in the same manner, acetylenic ketones of the type CR:C·COR′ (Abstr., 1910, i, 563) uniting readily with

amines to form amino-ketones of the types $R\cdot C(NHR''){:}CH\cdot COR'$ and $R\cdot C(NR''R'''){:}CH\cdot COR'$ respectively. These compounds are hydrolysed by acids with formation of an amine and a β-diketone.

When a primary amine acts on an acetylenic ketone, the principal reaction is one involving elimination of water. The mixtures rapidly blacken, however, and no definite condensation products have been isolated.

The following additive compounds have been prepared: α-cyclo-*Hexylamino-α-phenyl-Δ^α-penten-γ-one*, $C_6H_{11}\cdot NH\cdot CPh{:}CH\cdot COEt$, m. p. 100°. α-cyclo*Hexylamino-α-phenyl-Δ^α-hexen-δ-one*, m. p. 75°. *Benzylaminostyryl phenyl ketone*, $CH_2Ph\cdot NH\cdot CPh{:}CH\cdot COPh$, m. p. 100°, *α-Diethylamino-α-phenyl-Δ^α-penten-γ-one*, $NEt_2\cdot CPh{:}CH\cdot COEt$, m. p. 45°. *α-Diethylamino-α-phenyl-Δ^α-hexen-δ-one*, m. p. 40°. *α-Dipropylamino-α-phenyl-Δ^α-buten-γ-one*, $NPr_2^{\alpha}\cdot CPh{:}CH\cdot COMe$, m. p. 47°. *Diethylaminostyryl phenyl ketone*, $NEt_2\cdot CPh{:}CH\cdot COPh$, m. p. 63°; the corresponding *piperidyl* compound has m. p. 81°, and the *methylanilino*-compound, m. p. 87°. W. O. W.

Method of Characterising Certain Ureides [Carbamides]. Henry J. H. Fenton and William A. R. Wilks (*Proc. Camb. Phil. Soc.*, 1911, 16, 64).—Methylfuril, $C_{11}H_8O_4$ (Trans., 1903, **83**, 187; Abstr., 1906, ii, 489), is a very delicate reagent for detecting certain carbamides. Minute quantities of the reagent and of the carbamide are mixed on a filter-paper and treated with a drop of fuming hydrochloric acid; an intense blue coloration is developed after a few seconds. Positive results are given by substances containing the open-chain $\cdot NH\cdot CO\cdot NH_2$ (carbamide, methylcarbamide, benzylcarbamide, semicarbazide, oxaluric acid, biuret, and hydantoic acid); cyclic carbamides such as parabanic acid and hydantoin, and also oxamide, succinamide, *s*- and *as*-dimethylcarbamide do not respond to the test.

The positive result of the test given by allantoin is evidence in favour of the Grimaux formula: $NH_2\cdot CO\cdot NH\cdot CH<\begin{matrix} NH\cdot CO \\ | \\ CO-NH \end{matrix}$ (compare Biltz, Abstr., 1910, i, 594). C. S.

The Carbonyl Ferrocyanides. Their Extraction, Analysis, and Applications. Émile Lecocq (*Bull. Soc. chim. Belg.*, 1911, 25, 72—80).—In the extraction of ferrocyanides from the spent oxide of the gas purifiers, the filtrate from the insoluble calcium potassium ferrocyanide formed during the process contains any carbonylferrocyanide which may have been present in the spent oxide. Together with this carbonylferrocyanide there is also some calcium potassium ferrocyanide, calcium sulphate, calcium chloride, calcium thiocyanate, and potassium chloride. If this solution is concentrated to a gravity of 30° Bé., a granular mass separates, containing gypsum, the double ferrocyanide of calcium and potassium, and also calcium potassium carbonylferrocyanide. The latter salt deposits, because it is insoluble in the presence of the calcium salts contained in the mother liquor,

and it may be dissolved from the the collected precipitate by treatment with warm water. After recrystallisation it has the formula

$$CaKFe(CO)C_6N_6,5H_2O,$$

and forms straw-coloured crystals with a pearly lustre.

In addition to the reactions of this compound described by Muller (Abstr., 1899, ii, 616), the reactions with the following salts are described: Cuprous, zinc, mercurous, mercuric, silver, thallium, vanadium, stannous, and platinum salts. The heat of combustion is 622 Cals. per gram-molecule, and the heat of formation, – 133 Cals.

The method of determining the amount of carbonylferrocyanides in the spent oxide is described in detail. The calcium potassium salt is extracted, essentially according to the method indicated above, the calcium precipitated as carbonate, and the resulting solution of the potassium salt titrated with a standard solution of copper sulphate, the end of the reaction being indicated when the solution no longer gives a violet colour with ferric salts.

Generally speaking, carbonylferrocyanides are only found in the spent oxide when Laming's mixture has been used in the purifying boxes. It is present as the violet-coloured ferric salt to the extent of 0·4—1·1%. This violet salt gives printing inks and paints which are very stable towards the action of light. T. S. P.

Organic Amalgams. Substances with Metallic Properties Composed in part of non-metallic Elements. HERBERT N. McCOY and WILLIAM C. MOORE (*J. Amer. Chem. Soc.*, 1911, 33, 273—292).—Tetramethylammonium amalgam has been prepared by the electrolysis in the cold of solutions of tetramethylammonium chloride in absolute alcohol, using a mercury cathode. The amalgam exhibits certain physical properties of the metals to a high degree, and has a crystalline structure. It is lighter than mercury, but does not expand or become inflated at or below 10°, as does ammonium amalgam. In contact with cold air, it becomes coated with a white alkaline crust, due to oxidation. It reacts violently with water, producing hydrogen, colloidal mercury, and tetramethylammonium hydroxide; the phenomena observed during this reaction point to the existence of more than one active phase in the amalgam.

The amalgam acts on aqueous solutions of ammonium, sodium, potassium, and copper salts, and alcoholic solutions of copper and zinc salts, the alkylammonium group replacing the respective metals. With rubidium and cæsium salts the action is more violent than with potassium salts of equivalent concentration, but there is replacement, even in the case of the cæsium salts. The solution tension of the tetramethylammonium radicle is comparable with that of potassium, but it is much less than that of rubidium or cæsium.

The rate of formation of the tetramethylammonium ion from the amalgam, in contact with absolute alcohol, is about 5% per minute at 0°.

The *E.M.F.* of cells made up of the decinormal calomel electrode and the amalgam in contact with 0·5*N*-alcoholic or aqueous solutions of tetramethylammonium chloride was measured at 0°. With alcoholic solutions, the values obtained were 2·6 and 2·0 volts, whilst with

aqueous solutions the values were 2·4 and 1·7 volts. The two values obtained in each case probably correspond with two phases present in the amalgam.

The following salts were studied to see if amalgams could be formed. Methyl-, dimethyl-, trimethyl-, ethyl-, tetraethyl-, propyl- and butyl-ammonium chlorides; iodomethyltrimethylammonium iodide; aniline, dimethylaniline, phenylenediamine, pyridine, hydroxylamine, and hydrazine hydrochlorides; benzenediazonium chloride; tetraethyl-phosphonium, tetramethylstibium and trimethylsulphinium iodides. Of these, the monomethyl radicle yields an amalgam, and potential measurements show that it is less stable towards alcohol than towards water, in which respect it agrees with ammonium amalgam. The dimethylammonium radicle may possibly form an amalgam, as indicated by potential measurements, and this is also true of the tetraethyl-ammonium radicle, but the amalgams are very unstable. Of all the other substances investigated, a number gave faint indications of amalgam formation, but none gave results as positive as the three substances just mentioned.

The authors consider, therefore, that it is possible to prepare composite metallic substances from non-metallic constituent elements.

T. S. P.

Coal Tar Pitch. SIMON BERNUS (*Bull. Soc. chim. Belg.*, 1911, **25**, 7—40).—A study of coal tar pitch from the point of view of its use in briquetting coal dust.

From ordinary crude coal tar a yield of from 60—80% of residual pitch may be obtained, depending on the point at which distillation is stopped, and the product may be liquid, soft, or hard, according as more or less high boiling coal tar oil is left in it. A large number of high boiling hydrocarbons have been obtained by distilling pitch, but it is very doubtful whether these substances actually occur in it, and are not formed by pyrogenetic decomposition. On treatment with carbon disulphide, pitch dissolves to the extent of 80%. The insoluble matter resembles lampblack, is devoid of plastic properties, and is therefore of no value as an agglomerant. The portion soluble in carbon disulphide forms the plastic matter on which the agglomerating property of pitch depends. By treatment with solvents it can be separated into two fractions. Fraction *A* consists of a brown mass of buttery consistence, which liquefies at 45—60°, forming a black fluid which adheres strongly to any solid substance placed in it. This fraction appears to be largely composed of hydrocarbons.

Fraction *B* forms a solid, black, shining, crystalline powder, which melts at 200°, forming a slightly adherent varnish. It is soluble in carbon disulphide or tetrachloride, but its best solvent is the mixture of hydrocarbons forming fraction *A*. In briquetting coal dust, *A* probably plays the chief part as an agglomerant, whilst *B* solidifies at a comparatively high temperature, and thus assists in the formation of a hard, compact briquette.

The rest of the paper deals with the theory of briquetting, and points out that the formation of a good briquette depends primarily on the adjustment of temperature and pressure, so that each particle of

coal is completely enveloped in a layer of pitch, and the latter evenly distributed to fill all interstices between the particles of coal. In valuing pitch for briquetting purposes, the melting point (55—74°) and the total quantity of plastic matter (54—73%) are the chief factors to be considered. T. A. H.

Sabatier's Reduction and its Reversibility. ALADAR SKITA and H. RITTER (*Ber.*, 1911, **44**, 668—676).—The reduction of phenols, cyclic ketones, and alcohols by Sabatier's method is somewhat analagous to that of aliphatic compounds (Abstr., 1908, i, 855). Aromatic and reduced aromatic hydrocarbons are usually formed, especially when a rapid current of hydrogen is used. It is shown that benzene, *cyclo*hexane, and *cyclo*hexene are formed by the reduction of phenol and methyl*cyclo*hexane, and toluene by the reduction of *m*-cresol. *cyclo*Hexanone yields *cyclo*hexane and phenol, but little *cyclo*hexanol; 1-methyl*cyclo*hexan-2-ol yields methyl*cyclo*hexane and *o*-cresol together with unsaturated and aromatic hydrocarbons.

1-Methyl-Δ^1-*cyclo*hexen-3-ol gave methyl*cyclo*hexane and 1-methyl-*cyclo*hexan-3-one; *iso*phorone gave a hydrocarbon, C_9H_{18}, b. p. 140—143°, and *d*-pulegone gave *p*-cymene and *d*-*l*-menthane.

The reduction process consists of a number of equilibria as represented by the scheme:

Phenol $\rightleftarrows$ *cyclo*hexanone $\rightleftarrows$ *cyclo*hexanol $\longrightarrow$
*cyclo*hexene $\rightleftarrows$ *cyclo*hexane $\rightleftarrows$ benzene.

The aromatic hydrocarbons are formed by a process of dehydrogenation, and the amount tends to increase with the temperature, but it appears impossible to work under conditions such that this formation is entirely excluded.

1-*Chloro*-Δ^1-cyclo*hexene*, C_6H_9Cl, obtained by the action of phosphorus pentachloride on an absolute ethereal solution of *cyclo*hexanone, has b. p. 54—56°/20 mm. and D_{18}^{18} 1·0385. When reduced with sodium and methyl alcohol, it yields *cyclo*hexene.

Dihydro*iso*phorone and phosphorus pentachloride yield 5-*chloro*-1:1:3-*trimethyl*-Δ^5-cyclo*hexene*, $CMe_2<\begin{matrix}CH_2\cdot CHMe\\ CH{=\!=}CCl\end{matrix}>CH_2$, b. p. 70—71°/21 mm., and this on reduction with sodium and ethyl alcohol gives 1:1:3-trimethyl-Δ^5-*cyclo*hexene (*β*-*cyclo*geraniolene: compare Knoevenagel and Fischer, Abstr., 1897, i, 612), which can also be obtained by the reduction of the chloride of *iso*phorone with sodium and alcohol. The chloride obtained from 1-methyl*cyclo*hexan-2-ol (Gutt, Abstr., 1907, i, 509) has b. p. 156—158° and D_{18}^{18} 0·9676, and when reduced with zinc and an ethereal solution of hydrogen chloride yields the hydrocarbon, methyl*cyclo*hexane, C_7H_{14}, whereas when reduced with sodium and alcohol the chief product is methyl*cyclo*hexene.

The *chloride* obtained from *trans*-dihydro*iso*phorol and phosphorus pentachloride has b. p. 184°/756 or 76—78°/18 mm. and D_{18}^{18} 0·9281, and when reduced with zinc and an ethereal solution of hydrogen chloride yields the hydrocarbon, *trimethyl*cyclo*hexane*, C_9H_{18}, b. p. 137—138° and n_{17} 1·4327.

Sabatier's method of reduction is a convenient one for the preparation of saturated cyclic hydrocarbons; the compounds obtained appear

to be identical with the natural naphthenes, and so far the conversion of a 6-membered ring into a derivative of a 5-membered ring has not been observed, although such a molecular rearrangement occurs during reduction with hydriodic acid (Willstätter and Kametaka, Abstr., 1908, i, 401). J. J. S.

Compounds of Antimony Trichloride and Antimony Tribromide with Benzene. Boris N. Menschutkin (*Chem. Zentr.*, 1910, ii, 378; from *Izvista of the St. Petersburg Polytechnic*, **13**, 263).—Among the numerous systems of inorganic salts

$$(MgBr_2, MgI_2, AlCl_3, AlBr_3)$$

with aromatic hydrocarbons studied by the author, there was not one in which the formation of a molecular compound between the components could be proved. It was also found that the numerous alleged molecular compounds of aromatic hydrocarbons with halogen salts of aluminium could not exist within the temperature ranges studied. As similar additive compounds of antimony trichloride and antimony tribromide with aromatic hydrocarbons have been described, the author subjected these systems to a thorough thermometric study. It was found that these salts form with benzene the additive compounds $2SbCl_3,C_6H_6$ and $2SbBr_3,C_6H_6$. The thermometric analysis of these substances was made by the method of Alexéeff, and the composition of the isolated additive products determined by measuring the volume of benzene liberated by means of 20% hydrochloric acid. The author gives the freezing temperatures and eutectic points obtained for the systems he examined. In the case of the system antimony trichloride and benzene, the freezing diagram shows two eutectic points, at 1°, $SbCl_3,13C_6H_6$, and at 62°, corresponding with $SbCl_3,0·12C_6H_6$, and in between a distectic at 79°, the freezing point of the additive compound $2SbCl_3,C_6H_6$, which crystallises in very hygroscopic, rhombic plates. These compounds were erroneously given the formulæ $3SbCl_3,2C_6H_6$ and $3SbCl_3,C_6H_6$ (Smith and Davies, Trans., 1882, **41**, 411; Rosenheim and Stellmann, Abstr., 1902, ii, 68). In the case of the system antimony tribromide and benzene, the freezing diagram shows two eutectic points, at 4·5°, corresponding with $SbBr_3,51·6C_6H_6$, and at 85°, corresponding with $SbBr_3,0·18C_6H_6$; between the distectic at 92·5°, the freezing point of the additive compound $2SbBr_2,C_6H_6$, which crystallises in liquid, rhombic forms.

N. C.

Investigation of Systems of Substituted Benzenes with Antimony Chloride and Antimony Bromide. I. Halogen-substituted Benzene. Boris N. Menschutkin (*Chem. Zentr.*, 1910, ii, 379—380; from *Izvista of the St. Petersburg Polytechnic*, 13, 277. Compare preceding abstract).—In view of the great chemical differences which benzene derivatives exhibit, the author has determined the behaviour of these derivatives towards the halogen compounds of antimony; thus he examined a number of systems of halogen and nitro-derivatives of benzene with antimony trichloride and tribromide, and gives particulars of their freezing temperatures and eutectic points. The freezing diagram of the system antimony trichloride and chloro-

benzene consists of three curves which show a eutectic point at $-47°$, corresponding with $SbCl_3,44·5C_6H_5Cl$, and a transition point at $0°$, corresponding with $SbCl_3,2·56C_6H_5Cl$. Both components of the system form an additive compound, $SbCl_3,C_6H_5Cl$, which crystallises in long needles and decomposes at $0°$. The system antimony trichloride and bromobenzene is similar, with a eutectic point at $-32·5°$, corresponding with $SbCl_3,28·4C_6H_5Br$, and a transition point at $3°$, corresponding with $SbCl_3,1·48C_6H_5Br$; the additive compound,

$$SbCl_3,C_6H_5Br,$$

crystallises in needles, and in the absence of excess of antimony bromide has m. p. $6·5°$; the two additive compounds are isomorphous; inoculation with $SbCl_3,C_6H_5Cl$ prevents the crystallisation of $SbCl_3,C_6H_5Br$. The freezing diagram of the system $SbCl_3$ and iodobenzene is similar on the whole to the previous ones. It is distinguished from them by the fact that the additive product, $SbCl_3,C_6H_5I$, only separates exceptionally. Without inoculating with prepared crystals of this additive compound, a freezing diagram is obtained consisting of two curves which cut each other in the eutectic point at $-45°$, corresponding with $SbCl_5,2·62C_6H_5I$. Inoculation results in a diagram consisting of three curves with a eutectic point at $-34·5°$, corresponding with $SbCl_3,8·37C_6H_5I$, and a transition point at $-4·2°$, corresponding with $SbCl_3,1·5C_6H_5I$. The metastable additive compound, $SbCl_3,C_6H_5I$, forms long needles, m. p. $-2°$. The freezing diagram of the system antimony tribromide and chlorobenzene shows two curves, which cut at the eutectic point at $-47°$, corresponding with $SbBr_3,58C_6H_5Cl$, and that of the system tribromide and bromobenzene, two curves meeting at the eutectic point at $-32°$, corresponponning with $SbBr_3,37·5C_6H_5Br$. In the case of the system antimony tribromide and iodobenzene, the two curves cut at the eutectic point at $-32°$, corresponding with $SbBr_3,10·5C_6H_5I$. In all these systems only antimony trichloride showed a tendency to the formation of molecular compounds. Its tendency to combine with halogen-substituted benzene derivatives decreases regularly with the increase in the atomic weight of the substituting halogen atom. Four more systems of disubstituted derivatives of benzene were studied. The freezing diagram of the system antimony trichloride and *p*-dichlorobenzene consists of two curves which cut at the eutectic point at $39·5°$, corresponding with $SbCl_3,2·4C_6H_4Cl_2$. In the case of *p*-dibromobenzene the eutectic point is at $49·5°$, corresponding with

$$SbCl_3,0·54C_6H_4Br_2.$$

The diagrams for the systems of antimony tribromide and *p*-dichlorobenzene and *p*-dibromobenzene each show two curves with eutectic points at $48·5°$, corresponding with $SbBr_3,6·8C_6H_4Cl_2$, and at $65°$, corresponding with $SbBr_3,0·92C_6H_4Br_2$. Disubstituted benzenes do not form molecular compounds with antimony trichloride. N. C.

Examination of Systems of Substituted Benzenes with Antimony Trichloride. II. $SbCl_3$,$SbBr_3$ and Nitrobenzene. BORIS N. MENSCHUTKIN (*Chem. Zentr.*, 1910, ii, 381—382; from *Izvista of the St. Petersburg Polytechnic*, **13**, 411. Compare preceding abstracts).—The freezing diagram of the system antimony trichloride

and nitrobenzene shows three curves, of which the middle one, dividing the area of the solid molecular compound $SbCl_3,C_6H_5 \cdot NO_2$ from the liquid, does not always appear. This is because the compound has a very small velocity of crystallisation, and is only separated from the liquid by strong freezing. Apart from that, the diagram has two eutectic points, one at $-16 \cdot 5°$, corresponding with $SbCl_3,3C_6H_5 \cdot NO_2$, the other at $-6 \cdot 5°$, corresponding with

$$SbCl_3,0 \cdot 9C_6H_5 \cdot NO_2.$$

In between lies a very flat distectic at $-6°$, the freezing point of the additive compound $SbCl_3,C_6H_5 \cdot NO_2$, which crystallises in long needles.

The results for the system antimony trichloride and *m*-dinitrobenzene are analogous; there is a three-branched curve, but the middle one, corresponding with the compound $SbCl_3,m\text{-}C_6H_4(NO_2)_2$, is only realised exceptionally, as the compound is metastable. As a rule a diagram is obtained consisting of only two curves, which cut at the eutectic point at 1°, corresponding with $SbCl_3,0 \cdot 66C_6H_4(NO_2)_2$. If the fusion is inoculated with prepared crystals, a three-division freezing diagram is obtained with a eutectic point at 21°, corresponding with

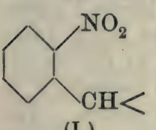
$$SbCl_3,0 \cdot 53C_6H_4(NO_2)_2,$$

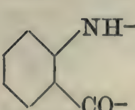
and a transition point at $28 \cdot 5°$, corresponding with

$$SbCl_3,0 \cdot 94C_6H_4(NO_2)_2.$$

The additive compound, $SbCl_3,C_6H_4(NO_2)_2$, forms rhombic crystals, m. p. $28 \cdot 5°$. The diagram for the system antimony tribromide and nitrobenzene shows two curves, cutting at a eutectic point at $-15°$, corresponding with $SbBr_3,2 \cdot 34C_6H_5 \cdot NO_2$; that for the system with *m*-dinitrobenzene has also two curves, the eutectic point being at $47 \cdot 5°$, corresponding with $SbBr_3,0 \cdot 84C_6H_4(NO_2)_2$. Of the two halogen compounds with antimony, only the trichloride shows a tendency to the formation of additive compounds, not only with halogen, but also with nitro-derivatives of benzene. N. C.

The Constitution of Anthranil. GUSTAV HELLER [and, in part, ERICH GRÜNTHAL] (*Chem. Zentr.*, 1910, ii, 975; from *Ber. K. Sächs. Ges. Wiss.*, *Math.-phys. Kl.*, 1910, 62, 46. Compare Abstr., 1908, i, 267; 1909 i, 832).—It is first shown that substances containing the group (I) in many reactions have a tendency to form substances of the type (II). In this way the formation of anthranil by the


(I.)


(II.)

reduction of *o*-nitrobenzaldehyde can be so explained that it is not analogous to the formation of methylanthroxan by the reduction of *o*-nitroacetophenone, and affords no argument as to the formula of anthroxan. Anthranil and methylanthroxan behave differently in nearly all their reactions. With aniline, anthranil condenses to form a *substance*, $C_{20}H_{15}O_3N$ or $C_{20}H_{17}O_3N$; this crystallises in needles, m. p. about 172°. From the solution in concentrated hydrochloric acid there separates a colourless *compound*, which forms needles, m. p. above 280°. By boiling the yellow condensation product for a quarter of an hour with acetic anhydride, the *acetyl* compound, $C_{22}H_{17}O_2N_3$, is obtained as needles, m. p. 186°. A similar condensation product is obtained from anthranil with *p*- and

o-toluidines; methylanthroxan does not react in a similar way with aniline. There is a slight formation of anthranil on heating anthroxanic acid with water at about 150°. At the same time there is formed an *acid*, m. p. 247°, soluble in sodium hydroxide; this is not identical with the *substance*, m. p. 245°, obtained on heating anthranil with water, which is insoluble in sodium hydroxide. When anthranil is boiled with water at 100°, it remains to a great extent unchanged; at a lower temperature, in addition to the compound, m. p. 245°, a *substance*, m. p. 285°, is formed, which is not basic and seems to be a mixture. That the action of anthranil towards 39% hydrochloric acid and sodium nitrite is analogous to that of methylanthroxan (formation of anthroxan dichloride and *o*-aldehydobenzenediazonium chloride) is probably to be explained by its tendency under the influence of strong mineral acids to suffer intermolecular change and react in the anthroxan form; by the action of concentrated hydrochloric acid a permanent desmotropic form is not produced. Anthroxanaldehyde is readily converted by dilute alkali into isatin; it immediately gives a blue indophenin reaction, but is very resistant towards strong sulphuric acid, separating to a great extent unchanged when water is added after the mixture has been kept for several days. N. C.

Nitrophenol Salts. ANTONI KORCZYNSKI (*Chem. Zentr.*, 1910, ii, 384; from *Kosmos*, 1910, **35**, *Radziszewski-Festband*, 461).—In continuation of previous work (Abstr., 1908, i, 977; 1909, i, 148, 639) the author notes the analogy between the colour of nitrophenol salts and the tendency of the nitrophenols to form abnormal salts with ammonia, namely, that nitrophenols which form yellow salts tend to form abnormal ammonium salts. The following *ammonium* salts of nitrophenols were prepared: $NO_2 \cdot C_7H_5I \cdot OH,NH_3$, at the ordinary temperature, and $NO_2 \cdot C_7H_5I \cdot OH,2NH_3$, at $-15°$, from 5-iodo-3-nitro-2-cresol; $NO_2 \cdot C_6H_2Br_2 \cdot OH,NH_3,C_4H_8N_2$(?), from 2-4-dibromo-6-nitrophenol at $-15°$; $NO_2 \cdot C_6H_2ClI \cdot OH,2NH_3$, from 4-chloro-6-iodo-2-nitrophenol at $-15°$; $NO_2 \cdot C_6H_2BrI \cdot OH,2NH_3$, from 4-bromo-6-iodo-2-nitrophenol at $-15°$. N. C.

Action of Aluminium Chloride on Benzene. ANNIE HOMER (*Proc. Camb. Phil. Soc.*, 1911, **16**, 65—66).—Benzene containing 25% of its weight of aluminium chloride is heated at 100° under a reflux condenser for ten to fourteen days. After treatment with water and hydrochloric acid, the product yields, in addition to the alkylbenzenes and phenol mentioned by Friedel and Crafts, a fraction, b. p. below 160°/10 mm., containing phenol and naphthalene. The formation of the latter is explained on the assumption that *o*-diethylbenzene is produced and subsequently dehydrogenised by the aluminium chloride. Naphthalene is not obtained when the experiment is performed in sealed tubes at 180° for two days. C. S.

The Action of Light on the Bromination of Tertiary *o*- and *p*-Butyltoluene and the Chlorination of *tert.*-Butylbenzene and *o*-Butyltoluene. JR. SALIBILL (*Bull. Acad. Sci. Cracow*, 1910, *A*, 606—608).—A mixture of bromine and *p*-butyltoluene in molecular

proportions was exposed to strong sunlight, when combination rapidly took place, giving a liquid that boiled at 156—159° under 32 mm. pressure. The bromine replaced a hydrogen atom of the side-chain, not in the ring.

o-Butyltoluene reacted with bromine slowly at first, more rapidly afterwards. The bromine did not enter the methyl group, a phenomenon attributed by the author to steric hindrance; instead, it replaced a hydrogen atom of the ring. Chlorine showed a similar behaviour.

tert.-Butylbenzene behaved towards bromine and chlorine like *o*-butyltoluene. E. J. R.

Cyclic Acetylenes. Phenylbutinene. Émile André (*Bull. Soc. chim.*, 1911, [iv], 9, 192—195).—The author proposes to generalise Tiffeneau's method for the preparation of aromatic olefinic hydrocarbons (Abstr., 1904, i, 872), and to prepare from the latter the corresponding acetylenes by bromination and decomposition of the bromides by alcoholic potassium hydroxide.

The application of this process to allylbenzene leads to the formation of phenylmethylacetylene, Ph·C⁝CMe.

Phenylbutylene, $CH_2Ph·CH_2·CH⁚CH_2$, prepared by the action of allyl iodide on magnesium benzyl chloride, contrary to Aronheim's statement (this Journ., 1874, 689), is readily converted by bromination in chloroform and the subsequent action of potassium hydroxide in alcohol into *phenylbutinene*, $CH_2Ph·CH_2·C⁝CH$, D^0 0·9391, b. p. 189—191°/758 mm., which is best purified through the sodium derivative, and then forms a colourless, highly refractive liquid. T. A. H.

A Convenient Method for the Reduction of Alcohols of the Diphenyl- and Triphenyl-methane Series. Alexei E. Tschitschibabin (*Ber.*, 1911, 44, 441—443).—The methods at present available for the reduction of the above-mentioned alcohols often yield poor results. The author finds that the reduction with hydriodic acid in acetic acid solution proceeds very readily, and gives almost quantitative yields.

The reduction is carried out by dissolving the alcohol in the smallest possible quantity of glacial acetic acid and adding an excess of a saturated solution of hydriodic acid in the same solvent; the mixture is heated to boiling, and the reduction product precipitated by pouring the solution into water containing sodium hydrogen sulphite, which removes the iodine formed in the reaction. Ethers and halogen derivatives may be reduced in the same manner.

The method has been applied for the preparation of triphenylmethane, diphenylmethane, and diphenylacetic acid from triphenylcarbinol, diphenylcarbinol, and benzilic acid respectively. F. B.

Dinaphthylmethanes and Some of their Derivatives. Alexei E. Tschitschibabin (*Ber.*, 1911, 44, 443—450).—The paper deals with the application of the author's method of reduction (preceding abstract) to the preparation of the three isomeric dinaphthylmethanes.

$\alpha\alpha$-Dinaphthylcarbinol, prepared by a modification of the method described by Schmidlin and Massini (Abstr., 1909, i, 561), is readily reduced to $\alpha\alpha$-dinaphthylmethane, m. p. 109° (compare Schmidlin and Huber, Abstr., 1910, i, 832); the latter compound is also produced, together with $\alpha\alpha$-dinaphthyl ketone, by distilling $\alpha\alpha$-dinaphthylcarbinol under diminished pressure: $2CH(C_{10}H_7)_2\cdot OH = CH_2(C_{10}H_7)_2 + CO(C_{10}H_7)_2$. The hydrocarbon is separated from the mixture by taking advantage of its insolubility in concentrated sulphuric acid. $\alpha\alpha$-Dinaphthylmethyl bromide is obtained by the action of hydrogen bromide on the carbinol in glacial acetic acid solution (compare Wheeler and Jamieson, Abstr., 1902, i, 763).

The interaction of magnesium α-naphthyl bromide and β-naphthaldehyde yields *$\alpha\beta$-dinaphthylcarbinol*, which crystallises in soft needles, m. p. 108—109°, dissolves in sulphuric acid with a blue colour, and, on reduction, yields *$\alpha\beta$-dinaphthylmethane*, crystallising in glistening, flat prisms, m. p. 96°. The carbinol forms with benzene a crystalline *compound*, $2CH(C_{10}H_7)_2\cdot OH,C_6H_6$, which decomposes at 78° into its constituents.

$\alpha\beta$-Dinaphthylmethyl bromide, $CH(C_{10}H_7)_2Br$, prepared from the carbinol and hydrogen bromide in glacial acetic acid solution, crystallises in needles, m. p. 123—123·5°.

By the interaction of magnesium β-naphthyl bromide and ethyl formate, $\beta\beta$-dinaphthylcarbinol is obtained as an oil, which crystallises when left over sulphuric acid (compare Schmidlin and Huber, *loc. cit.*); on treatment with hydrogen bromide in acetic acid solution, it yields *$\beta\beta$-dinaphthylmethyl bromide*, which forms a crystalline powder, m. p. 168—169°, gives a violet coloration with sulphuric acid, and yields $\beta\beta$-dinaphthylmethane when reduced with hydriodic acid.

The $\beta\beta$-dinaphthylmethane thus obtained has m. p. 93°, and is identical with the hydrocarbon prepared by Richter (Abstr., 1881, 281) by the reduction of the corresponding ketone.

By reducing di-β-naphthaxanthone, $C_{10}H_6{<}{}^{CO}_{O}{>}C_{10}H_6$, with hydriodic acid, Claus and Ruppel (Abstr., 1890, 511) obtained a hydrocarbon to which they assigned the formula of $\alpha\alpha$-dinaphthylmethane; Schmidlin and Huber consider it to be the $\alpha\beta$-compound. The hydrocarbon differs, however, in properties from the three isomeric dinaphthylmethanes described above, so that its constitution remains undetermined. F. B.

Halogen Derivatives of Triphenylmethane. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1911, **44**, 450—459).—A further application of the author's method of reduction (preceding abstracts) to the preparation of the halogen derivatives of triphenylmethane.

p-Chlorotriphenylcarbinol, previously obtained by Gomberg and Cone (Abstr., 1906, i, 822), crystallises from light petroleum in large cubes, m. p. 85°. On reduction it yields *p-chlorotriphenylmethane*, which crystallises in two forms, glistening needles, m. p. 59·5°, and large, transparent crystals, m. p. 54°. The latter form is unstable, and is transformed, when kept, into the less fusible modification.

o-*Chlorotriphenylcarbinol*, prepared by the action of magnesium phenyl bromide on methyl *o*-chlorobenzoate, forms a crystalline powder, m. p. 91—92°, gives an orange-yellow coloration with concentrated sulphuric acid, and yields o-*chlorotriphenylmethyl bromide*, m. p. 118—121°. The bromide gives, on reduction, o-*chlorotriphenylmethane*, which crystallises in short prisms, m. p. 77°, and forms a crystalline *compound* with benzene; this decomposes at 40° into its constituents.

p-*Bromotriphenylmethyl bromide*, prepared from the corresponding carbinol (Cone and Long, Abstr., 1906, i, 424), has m. p. 132—134°, and is readily reduced to p-*bromotriphenylmethane*, which resembles the *p*-chloro-compound in being dimorphous. The stable modification, obtained by inoculating a solution of *p*-bromotriphenylmethane in light petroleum with the stable form of the *p*-chloro-compound, crystallises in glistening needles, m. p. 82·5°. The second modification has m. p. 68°, and is more soluble than the stable form. *p*-Bromotriphenylmethane differs from the ortho- and meta-isomerides in not forming a crystalline compound with benzene.

o-*Bromotriphenylcarbinol*, obtained by the interaction of magnesium phenyl bromide and methyl *o*-bromobenzoate, crystallises from hot glacial acetic acid in soft leaflets, m. p. 158°, and gives an orange-yellow coloration with sulphuric acid.

o-*Bromotriphenylmethyl bromide* forms a coarsely crystalline powder, m. p. 120—125° (decomp.), and yields, on reduction, o-*bromotriphenylmethane*; the latter crystallises in short, glistening prisms, m. p. 81°, and forms a crystalline *compound* with benzene, m. p. 45° (decomp.).

m-*Bromotriphenylmethyl bromide*, obtained by the action of hydrobromic acid on *m*-bromotriphenylcarbinol (Cone and Long, *loc. cit.*), separates from light petroleum in glistening crystals, m. p. 145—146°; it is deposited from its solutions in glacial acetic acid in the form of white granules, m. p. 75°, which apparently contain acetic acid.

m-*Bromotriphenylmethane*, prepared from the corresponding bromide by reduction, separates from benzene in large, crystalline granules of the composition $C_{19}H_{15}Br,C_6H_6$; these have m. p. 55°, and, on keeping, are slowly transformed into a viscid oil; when heated to 80° the benzene of crystallisation is lost, *p*-bromotriphenylmethane separates as an oil which could not be obtained in a crystalline form.

p-Iodotriphenylcarbinol, prepared by the interaction of magnesium phenyl bromide and methyl *p*-iodobenzoate, is converted by the action of acetyl chloride into the carbinyl chloride, m. p. 123°: Gomberg and Cone (*loc. cit.*) give 125°.

p-*Iodotriphenylmethane* crystallises in yellow needles, m. p. 81·5°.

Tri-*p*-bromotriphenylmethane, prepared by reducing tri-*p*-bromotriphenylmethyl ethyl ether, has m. p. 115° (compare Fischer and Hess, Abstr., 1905, i, 205). F. B.

a-**Methylanthracene.** OTTO FISCHER and A. SAPPER (*J. pr. Chem.*, 1911, [ii], **83**, 201—208).—*a*-Methylanthracene and its *β*-isomeride, which both crystallise in white leaflets, are stated to have approximately the same m. p., and yield methylanthraquinones also having

nearly the same m. p. Since the two hydrocarbons are produced by the distillation of very different natural substances with zinc dust, it is desirable to have a certain method of distinguishing between them. The authors obtain a very poor yield of impure α-methylanthracene by Birukoff's method of distilling 4-hydroxy-1-methylanthraquinone with zinc dust, the main product being anthracene. α-Methylanthracene is conveniently obtained by distilling 4-chloro-1-methylanthraquinone (Heller and Schülke, Abstr., 1908, i, 994) with zinc dust at a very low red heat; it has m. p. 85—86°, crystallises in long, white needles, is much more soluble in most solvents than anthracene or β-methylanthracene, forms a blue fluorescent solution in alcohol, and yields a *picrate*, red needles, m. p. 113—115°. α-Methylanthraquinone, m. p. 170—171°, does not lose its methyl group by distillation with zinc dust, and differs from β-methylanthraquinone by rapidly reddening on exposure to light. It is oxidised by dilute nitric acid at 160° to anthraquinone-1-carboxylic acid, which develops a rose coloration when heated with soda-lime; anthraquinone-2-carboxylic acid turns blue under similar conditions. 4-*Chloro*-1-*methylanthracene*, $C_{15}H_{11}Cl$, m. p. 112°, obtained by boiling 4-chloro-1-methylanthraquinone with zinc dust and aqueous ammonia, does not lose its halogen by distillation with zinc dust. 4-*Methoxy*-1-*methylanthraquinone*, m. p. 128°, yellow needles, obtained from 4-chloro-1-methylanthraquinone and methyl-alcoholic potassium hydroxide at 100° under pressure, reddens in light, and is converted into 4-hydroxy-1-methylanthraquinone by glacial acetic and concentrated hydrochloric acids at 100° under pressure. C. S.

Aliphatic Nitro-compounds. IX. Action of Phenylcarbimide on Sodium Nitromethane and Nitroethane. WILHELM STEINKOPF and H. M. DAEGE (*Ber.*, 1911, **44**, 497—502. Compare this vol., i, 4).—When sodium nitromethane and phenylcarbimide in benzene solution are set aside for some weeks, nitroacetanilide and a little malonanilide are formed (Michael, Abstr., 1905, i, 195). Reaction is quicker when the components are warmed for an hour on the water-bath; in both cases a further investigation has proved that *s*-diphenylcarbamide and triphenylbiuret are also formed. The last is converted on boiling with potassium hydroxide into diphenylcarbamide, and its formation is obviously due to the action of excess of phenylcarbimide on diphenylcarbamide. The constitution of nitroacetanilide was confirmed by its conversion into nitroacetic acid by boiling with strong aqueous potassium hydroxide.

Sodium nitroethane and phenylcarbimide only yield traces of the sodium salt of α-nitropropionanilide, the main products here being *s*-diphenylcarbamide and triphenylbiuret. In other experiments, particularly those made with fresh phenylcarbimide, triphenyl*iso*cyanurate, $C_3N_3O_3Ph_3$, together with nitrogen and some diphenylcarbamide are formed. This reaction is in opposition to Michael's theory (*loc. cit.*) that the course of change followed is that in which a maximum of chemical neutrality is attained. E. F. A.

Action of Nitrous Acid on Dinitrodialkylanilines. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 820—822).—The substance, m. p. 175—176°, obtained by Hantzsch by the action of nitric acid, D 1·3, on dimethylaniline, and described as 3 : 4-dinitrodimethylaniline (Abstr., 1910, i, 475), is proved to be 2 : 4-dinitromethylaniline ; its mixture with the true 3 : 4-dinitrodimethylaniline, m. p. 176°, causes a large depression of the m. p. The production of the dinitromethylaniline is due to the elimination of one methyl group by the nitrous acid formed during the nitration; in fact, 2 : 4-dinitrophenylmethylnitrosoamine is produced when a solution of dimethylaniline in ten volumes of nitric acid, D 1·3, is kept overnight. When, however, carbamide is added to the nitric acid to decompose the nitrous acid formed, the main product of the nitration of dimethylaniline is 2 : 4-dinitrodimethylaniline, m. p. 87°. By treating a solution of this substance in five times its weight of nitric acid, D 1·3, with sodium nitrite, 2 : 4-dinitrophenylmethylnitrosoamine is obtained, from which 2 : 4-dinitromethylaniline is produced by boiling with acetic acid. Precisely similar reactions are exhibited by 2 : 4-dinitrodiethylaniline and 2 : 4-dinitrodipropylaniline.

The action of nitrous acid on 3 : 4-dinitrodialkylanilines in dilute sulphuric acid also results in the elimination of one alkyl group and the formation of a nitrosoamine ; thus, 3 : 4-dinitrodiethylaniline yields a pale yellow *nitroso*-compound, m. p. 79—80°. Also, the same behaviour is shown by 3 : 6-dinitrodiethylaniline, which is converted by nitrous acid into a yellow *nitroso*-compound, m. p. 69°, from which 3 : 6-dinitroethylaniline is produced almost instantly by boiling acetic acid. 3 : 6-Dinitrodimethylaniline behaves in a similar manner.

C. S.

A New Preparation of Diphenylmethylamine (Benzhydrylamine). HEINRICH BILTZ and KARL SEYDEL (*Ber.*, 1911, **44**, 411—413).—Diphenylmethylamine is readily prepared by heating 5 : 5-diphenylhydantoin (Biltz and Rimpel, Abstr., 1908, i, 462) at 230—300° with an excess of potassium hydroxide and a small quantity of water ; it has b. p. 303·6° (corr.). The *picrate*, $C_{19}H_{16}O_7N_2$, crystallises in deep yellow needles, m. p. 205—206° (decomp.).

5 : 5-Diphenylthiohydantoin, when fused with potassium hydroxide at 300°, is quantitatively converted into diphenylmethylamine ; at 260°, 5 : 5-diphenylhydantoin is produced simultaneously.

An improved method for the preparation of the last-mentioned compound is described.

F. B.

Doubly Linked Carbon Atoms and the Carbon–Nitrogen Linking. V. Fission of Quaternary Ammonium Salts by Nascent Hydrogen. VI. Formation of Mixed Tertiary Amines. VII. Relative Mobility of Allyl-, Benzyl-, and Cinnamyl- in the Fission of Quaternary Ammonium Salts by Reduction. HERMANN EMDE [with HANS SCHELLBACH in VI and VII] (*Arch. Pharm.*, 1911, **249**, 106—111, 111—117, 118—122. Compare Abstr., 1909, i, 565, 708, 709).—Phenylbenzyldimethyl-

ammonium chloride (*aurichloride*, m. p. 97—98°, decomp.; *platinichloride*, m. p. 181°, decomp.) reduces normally (*loc. cit.*) with sodium amalgam in water, giving dimethylaniline and toluene, but when the reduction is effected in alcohol, toluene is in part replaced by benzyl ethyl ether. It is probable that in presence of alcohol the substituted ammonium chloride breaks up, first, into dimethylaniline and benzyl chloride, and that the latter then reacts with sodium ethoxide. The general method of carrying out the reaction and isolating the products is described.

The fission by reduction method may be applied to the preparation of mixed tertiary amines in the following way (compare Emmert, Abstr., 1909, i, 376).

Tribenzylmethylammonium iodide, m. p. 184°, gives a *cadmi-iodide*, m. p. 238°, and with silver chloride the corresponding *chloride*, m. p. 202°; the *platinichloride* has m. p. 209°, and the *aurichloride*, m. p. 188° (decomp.). The iodide itself on reduction with sodium amalgam in aqueous alcohol gives benzyl ethyl ether and dibenzylmethylamine (Abstr., 1909, i, 709); the latter reacts with allyl iodide to form *dibenzylmethylallylammonium iodide*, m. p. 149°, which on reduction gives *benzylmethylallylamine*, b. p. 255—256°/760 mm. (*platinichloride*, m. p. 139°). From this amine, *benzylmethylallylpropylammonium chloride*, m. p. 279°, was prepared, and this on reduction furnished *methylallylpropylamine*, b. p. 171—172°/765 mm., which gives a *platinichloride*, m. p. 144° (decomp.), and an oily *aurichloride*.

The foregoing work shows that in the fission of a quaternary ammonium compound containing both allyl- and benzyl- the latter is perferably removed from the *N*-atom, and the following results show that cinnamyl-, like benzyl-, is more mobile than allyl- in this connexion (compare von Braun, Abstr., 1907, i, 899; Wedekind and Paschke, Abstr., 1910, i, 372). *Dicinnamyldiethylammonium chloride*, on reduction with sodium amalgam in water, furnishes phenylpropylene and *cinnamyldiethylamine*, b. p. 263—265°/765 mm. (*platinichloride*, m. p. 208°, decomp.), which combines with allyl iodide to give *cinnamyldiethylallylammonium iodide*, m. p. 106° (*platinichloride*, m. p. 157°), and this on reduction with sodium amalgam in water yields diethylallylamine (platinichloride, m. p. 166°, not 128—130°, as stated by Liebermann and Paal, Abstr., 1883, 908). T. A. H.

Tetracinnamyl- and Tetrabenzyl-ammonium. HERMANN EMDE (*Arch. Pharm.*, 1911, **249**, 93—106. Compare Abstr., 1909, i, 708).—It is now well-established that there is a difference in function between the first three and the fifth valencies of a nitrogen atom, but it is not yet certain whether the fourth valency is of the same type as the first three, or has some special function. With a view to throwing light on this point, the author is investigating the formation and stability of substituted ammonium compounds containing four similar organic radicles. Tetracinnamylammonium salts are now described, but tetrabenzylammonium compounds could not be obtained.

[With HANS SCHELLBACH.]—Tetracinnamylammonium chloride, m. p. 199°, may be obtained by melting together tricinnamylamine and cinnamyl chloride and washing the product with ether. A process for its

isolation from the mixed amines formed by the action of ammonia on cinnamyl chloride is also described. It is almost insoluble in water, but readily soluble in acetone or alcohol. It is stable towards alkalis, but is decomposed by silver hydroxide, suspended in alcohol, giving *tetracinnamylammonium hydroxide*, which crystallises in colourless, compact rods, sinters at 146°, solidifies again at 165°, and re-melts at 170°; the hydroxide absorbs carbon dioxide from the atmosphere, and on heating decomposes at 150—175°/20—30 mm., yielding a thick, yellow distillate, b. p. 184°, which rapidly resinifies.

Cinnamyltrimethylammonium chloride, m. p. 156°, was obtained crystalline; it does not give the corresponding hydroxide by the action of silver hydroxide, as decomposition ensues with the formation of trimethylamine.

Attempts to prepare tetrabenzylammonium chloride by various methods, including Brunner's, confirmed Marquardt's experience that this substance cannot be obtained. Its non-formation is probably a special case of "steric hindrance." T. A. H.

Red and White Silver Salts of 2 : 4 : 6-Tribromophenol. HENRY A. TORREY and WILLIAM H. HUNTER (*J. Amer. Chem. Soc.*, 1911, 33, 194—205).—In an earlier paper (Abstr., 1907, i, 1030) the authors described red and white isomeric silver salts of 2 : 4 : 6-tribromophenol. This observation was confirmed by Hantzsch and Scholtze (Abstr., 1908, i, 17), who also described similar derivatives of 2 : 6-dibromo-*p*-cresol.

It has now been found that 2 : 4 : 6-tribromoresorcinol methyl ether and 3 : 4 : 6-tribromoguaiacol also yield red and white silver salts, but in these cases the red salts undergo transformation into the white isomerides too rapidly to permit of their isolation.

When solid potassium hydroxide is added to a solution of 3 : 4 : 6-tribromoguaiacol in dry acetone, a yellow *potassium* derivative is produced, which is immediately decolorised on addition of water. On adding a solution of silver nitrate in acetone to the acetone solution of the salt, a red precipitate is produced, which rapidly turns black.

The two silver salts of 2 : 4 : 6-tribromophenol do not show any difference in their behaviour towards acids, alkali hydroxides, alkyl iodides, or other reagents. It is considered probable that the change of the red salt into the white modification is due to tautomerism, the white salt being the stable form with the ordinary benzenoid formula, and the red salt the labile form with the ortho-quinonoid constitution, $O:C_6H_2Br_2:BrAg$. Hantzsch, however, has raised objections to the latter formula, and has stated that if silver could behave in this way, mercury ought to show even greater tendency to form such compounds, and should, therefore, give coloured salts, whereas the mercuric salts of tribromophenol and other phenols obtained by Hantzsch and Auld (Abstr., 1906, i, 471) were white. It is pointed out, however, that mercuric salts do not resemble silver salts so closely as do mercurous salts, and, as the result of experiments, it has been found that 2 : 4 : 6-tribromophenol and 2 : 4 : 6-tribromoresorcinol both yield yellow *mercurous* salts, and tri-iodophenol, an orange *mercurous* salt. Yellow precipitates were also obtained on the addition of mercurous

nitrate to alcoholic solutions of tribromoresorcinol methyl ether and tetrabromoguaiacol.

2 : 4 : 6-*Tribromoresorcinol dimethyl ether*, m. p. 68—69°, forms a crystalline powder. E. G.

Salt Formation by Aminophenols. WILHELM SUIDA (*J. pr. Chem.*, 1911, [ii], 83, 233—242).—The problem of the formation of salts by amphoteric organic substances has been approached by dissolving equivalent quantities of an aminophenol and of an aromatic amino-acid in just sufficient hot water, heating the solution rapidly to boiling, filtering, cooling, and examining the crystals obtained. The unexpected result has been obtained, that of the three aminophenols only the ortho-compound forms salts with anthranilic acid (orange-red prisms, decomp. below 100°), *m*-aminobenzoic acid (stout, red prisms, decomp. 100°), and *p*-aminobenzoic acid (brownish-red prisms, m. p. 139°). The explanation suggested, namely, that salts of the type $C_6H_4<{-O-\atop NH_3\cdot O}>C(OH)\cdot C_6H_4\cdot NH_2$ are formed, is supported by the fact that again only *o*-aminophenol forms salts with benzoic acid (yellowish-brown or brownish-red prisms which lose benzoic acid at 100°), phenylacetic acid (colourless leaflets, m. p. 130—131°), and sulphanilic acid (brownish-red prisms, nearly unchanged at 250°). o-*Aminophenyl formate* has m. p. 119—120°; all of these salts can be recrystallised from boiling water; when animal charcoal is added, however, the substance separates in two distinctly different crystalline forms. The salts lose weight continuously at 100—105°, owing partly to the volatilisation of the salt itself, partly to the escape of the more volatile constituent; oxazoles are not formed. *o*-Aminophenol does not form additive compounds of the above type with other substances containing a carbonyl group. It condenses, under the conditions mentioned, with methyl oxlate to form o-*aminophenol* o-*hydroxyphenyloxamate*, $C_{14}H_{14}O_5N_2$, and with acetylacetone to form a *substance*, m. p. 186—187°, which is probably $OH\cdot C_6H_4\cdot N\colon CMe\cdot CH_2\cdot COMe$. C. S.

Phenyl Ether and Some of its Derivatives. ALFRED N. COOK (*J. Amer. Chem. Soc.*, 1911, 33, 254—255).—An addendum to the earlier paper (Abstr., 1910, i, 731).

Tetrabromo-p-*tolyl ether*, $O(C_6H_2MeBr_2)_2$, b. p. 310—330°/40 mm., is obtained by the action of bromine in direct sunlight on a warm solution of *p*-tolyl ether as a light yellow, viscous substance which crystallises on cooling. A more highly brominated derivative could not be obtained. Dibromo-*p*-tolyl ether was obtained in small yield by adding bromine gradually to *p*-tolyl ether heated at 150°.

The results of experiments on the action of bromine on *o*-tolyl ether were not satisfactory, but were sufficient to show that the bromine enters the nucleus and not the side-chain. E. G.

Attempts to Prepare Optically Active Phosphorus Compounds. FRITZ EPHRAIM (*Ber.*, 1911, 44, 631—637. Compare Caven, Trans., 1902, 81, 1362; Luff and Kipping, *ibid.*, 1909, 95, 1993; Meisenheimer and Lichtenstadt, this vol., i, 344).—Attempts to resolve

compounds of the types $NH_2\cdot PO(ONa)\cdot OPh$ and $NH_2\cdot PS(ONa)\cdot OPh$ into optically active components were unsuccessful. A better yield of Stokes' diphenyl aminophosphate (Abstr., 1893, i, 315) is formed when an excess of phosphoryl chloride is used. The ester reacts with a hot boiling solution of barium hydroxide (equal weights of ester and crystallised hydroxide in 100 c.c. of water), yielding the *barium* salt of phenyl aminophosphoric acid, $[NH_2\cdot PO(OPh)\cdot O]_2Ba,H_2O$, which crystallises in microscopic needles readily soluble in water. The corresponding *cinchonine* salt, $NH_2\cdot PO(OPh)\cdot OH,C_{19}H_{22}ON_2$, crystallises in minute needles, m. p. 194°, and then in flat prisms, but both fractions had the same value for $[\alpha]_D$, namely, $+11\cdot5°$.

The *chloride*, $PSCl(OPh)_2$, prepared by the addition of sulphur to the chloride of diphenyl phosphite at 200—300°, crystallises from alcohol in brilliant, colourless, glistening needles, m. p. 68°. It is decomposed when boiled with water, and its alcoholic solution reacts with concentrated aqueous ammonium hydroxide, yielding the *diphenyl aminothiophosphate*, $NH_2\cdot PS(OPh)_2$, which crystallises in thin, rhombic leaflets, m. p. 112°. This ester is hydrolysed by alcoholic sodium hydroxide solution, yielding the *sodium* salt,

$$OPh\cdot PS(NH_2)\cdot ONa,2H_2O,$$

which dissolves readily in both alcohol and water; its aqueous solution yields precipitates with silver nitrate, lead acetate, and copper sulphate. The corresponding *cinchonine* salt, $C_{25}H_{30}O_3N_3SP$, obtained by the action of the sulphate of the base on the sodium salt in absolute alcoholic solution, forms a syrupy mass, and has $[\alpha]_D +11\cdot06°$.

J. J. S.

p-Aminothiophenol [*p*-Aminophenyl Mercaptan]. III. THEODOR ZINCKE and P. JÖRG (*Ber.*, 1911, **44**, 614—626. Compare Abstr., 1909, i, 789; this vol., i, 39).—A *dye*, $C_{14}H_{15}N_2S_2Cl$, which crystallises in violet-black, lustrous plates and yields deep blue alcoholic solutions, is formed by the oxidation of an alcoholic solution of *p*-methylthiolaniline (*p*-aminophenyl methyl sulphide) with a $1\cdot5N$-aqueous solution of ferric chloride. The free *base*, prepared by the action of dilute ammonia on the hydrochloride, forms a heavy, brownish-red, flocculent mass, which readily undergoes decomposition when in solution or when dried. The dye is decomposed when left in contact with dilute hydrochloric acid for some time, and yields *p*-methylthiolaniline and reacts with a methyl-alcoholic solution of *p*-toluidine, yielding a compound, $SMe\cdot C_6H_4\cdot N:C_6H_2(NH\cdot C_7H_7)_2:N\cdot C_7H_7$, which crystallises from toluene in dark reddish-brown, glistening plates, m. p. 238°. The *leuco*-compound, $C_{14}H_{16}N_2S_2$, obtained by reducing the dye with stannous chloride, crystallises from dilute alcohol in slender, colourless needles resembling asbestos, and has m. p. 105°. The *hydrochloride* crystallises from alcohol in colourless plates, and both base and hydrochloride are readily oxidised to the dye by means of ferric chloride or nitrous acid. The *acetyl* derivative, $C_{16}H_{18}ON_2S_2$, crystallises from dilute acetic acid in glistening prisms, m. p. 155°, and the *trimethylammonium iodide*, $C_{17}H_{23}N_2S_8I$, forms a colourless, crystalline powder, m. p. 186—190° (decomp.). The leuco-base is

regarded as a derivative of *p*-phenylenediamine, and is given the formula: $\overset{4}{N}H_2{\cdot}C_6H_3(\overset{2}{S}Me){\cdot}\overset{1}{N}H{\cdot}C_6H_4{\cdot}\overset{4'}{S}Me$, and the corresponding dye the structural formula: $HCl,NH{:}C_6H_3(SMe){:}N{\cdot}C_6H_4{\cdot}SMe$. The para-formula is preferred, as the leuco-compound does not give the reactions characteristic of an orthodiamine, for example, it does not yield an azimino-derivative with nitrous acid, but this formula necessitates the assumption of the wandering of a ·SMe-group during the oxidation of the methylthiolaniline to the dye (compare Bamberger, Abstr., 1901, i, 140; Zincke, 1901, i, 330; Kumazai and Wolffenstein, 1908, i, 159). When oxidised with hydrogen peroxide, the acetyl derivative yields the *disulphone*, $NHAc{\cdot}C_6H_3(SO_2Me){\cdot}NH{\cdot}C_6H_4{\cdot}SO_2Me$, which crystallises from nitrobenzene in yellow needles, m. p. 273—275° (decomp.).

The leuco-compound reacts with a glacial acetic acid solution of phenanthraquinone, yielding

$$C_6H_4{<}{}^{C_6H_4}_{CO}{>}C{:}N{\cdot}C_6H_4(SMe){\cdot}NH{\cdot}C_6H_4{\cdot}SMe$$

in the form of a dark carmine-red, crystalline powder, m. p. 281°. It has feebly basic properties, and its salts have an intense deep-blue colour. The leuco-base also reacts with carbon disulphide in the presence of alcohol at 100°, yielding a thiocarbamide derivative,

$$CS[NH{\cdot}C_6H_3(SMe){\cdot}NH{\cdot}C_6H_4{\cdot}SMe]_2,$$

which crystallises from glacial acetic acid in small, colourless needles, m. p. 160°. The compound,

$$C_6H_4{<}{}^{CH_2}_{CH_2}{>}N{\cdot}C_6H_3(SMe){\cdot}NH{\cdot}C_6H_4{\cdot}SMe,$$

obtained by shaking the leuco-base with a chloroform solution of *o*-xylylene bromide for two days, crystallises from alcohol in colourless needles, m. p. 139°.

Azoxyphenyl methyl sulphone, $ON_2(C_6H_4{\cdot}SO_2Me)_2$, prepared by oxidising *p*-methylthiolaniline with hydrogen peroxide, crystallises from glacial acetic acid in yellow prisms, m. p. 264°.

The dye formed by the oxidation of *p*-anisidine with ferric chloride has not been obtained in a pure state. *p*-Aminothiophenol is not readily oxidised, and does not yield a dye analogous to that obtained from *p*-aminophenol (Willstätter and Piccard, Abstr., 1909, i, 517). It is suggested that the leuco-compound derived from the dye from *p*-aminophenol is 4-amino-3 : 4′-dihydroxydiphenylamine.

J. J. S.

Action of Thionyl Chloride and of Sulphur Dioxide on Magnesium Alkyl Halides. BERNARDO ODDO (*Gazzetta*, 1911, 41, i, 11—16. Compare Strecker, also Grignard and Zorn, Abstr., 1910, i, 532).—Thionyl chloride reacts with magnesium ethyl iodide, forming ethyl sulphide, and with magnesium phenyl bromide it yields phenyl sulphide, in addition to small quantities of phenylsulphoxide and diphenyl.

Sulphur dioxide and magnesium phenyl bromide react, producing phenyl sulphide, as well as small quantities of phenylsulphoxide and diphenyl.

R. V. S.

Sulphur Derivatives of *p*-Cresol. THEODOR ZINCKE and J. KEMPF (*Ber.*, 1911, **44**, 413—424).—*Potassium* 5-*bromo*-p-*cresol*-3-*sulphonate*, $HO\cdot C_6H_2MeBr\cdot SO_3K$, prepared by the addition of a mixture of bromine and glacial acetic acid to an aqueous solution of potassium *p*-cresol-3-sulphonate, forms lustrous, white leaflets; the *methyl* ester crystallises in long, prismatic needles, m. p. 79—80°; the *ethyl* ester in stout prisms, m. p. 54—55°.

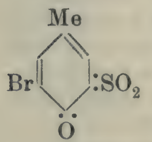
5-*Bromo*-p-*cresol*-3-*sulphonyl chloride*, $OH\cdot C_6H_2MeBr\cdot SO_2Cl$, obtained by treating the corresponding potassium salt with chlorosulphonic acid, crystallises in needles, m. p. 94—95°. The action of phosphorus pentachloride or phosphoryl chloride on the potassium salt yields, besides the sulphonyl chloride, an *ester* having the formula

$$SO_2Cl\cdot C_6H_2MeBr\cdot O\cdot POCl_2,$$

and crystallising in colourless prisms, m. p. 147°.

The *acetyl* derivative of 5-bromo-*p*-cresol-3-sulphonyl chloride forms lustrous, apparently monoclinic prisms, m. p. 84—85°.

When anhydrous potassium acetate is added to solutions of the sulphonyl chloride in acetone or ether, a yellow coloration is produced, due to the removal of hydrogen chloride and the formation of 5-*bromo*-o-*toluosulphonoquinone* (annexed formula).



A similar action takes place on the addition of ammonia to an alcoholic solution of the sulphonyl chloride, but the sulphonoquinone thus produced unites with the alcohol to form an ester of the sulphonic acid. By evaporating the yellow acetone or ethereal solutions, a white, crystalline powder, consisting of the polymeric form of the sulphonoquinone, is obtained; the same substance is also produced by the action of chlorosulphonic acid on 5-bromo-*p*-cresol-3-sulphonyl chloride.

On reduction with zinc dust and hydrochloric acid in alcoholic solution, the sulphonyl chloride yields 5-*bromo*-p-*cresol* 3-*mercaptan*, $OH\cdot C_6H_2MeBr\cdot SH$, crystallising in long, lustrous, silky needles, m. p. 32—33°; the *diacetyl* derivative is a liquid; the *dibenzoyl* derivative forms colourless needles, m. p. 93—94°.

5-*Bromo*-p-*cresol* 3-*disulphide*, $S_2(C_6H_2MeBr\cdot OH)_2$, prepared by oxidising the mercaptan with ferric chloride, crystallises in lustrous, pale yellow needles, m. p. 76—77°; the *dibenzoyl* derivative forms colourless needles, m. p. 130—131°.

On methylation with methyl iodide and sodium methoxide in methyl-alcoholic solution, the mercaptan is converted into 5-*bromo*-3-*methylthiol*-p-*cresol*, $OH\cdot C_6H_2MeBr\cdot SMe$, which forms a colourless, strongly refractive oil, b. p. 162—163°/13—14 mm., yields an *acetyl* derivative, crystallising in colourless needles, m. p. 51—52°, and, when treated with bromine in chloroform solution, gives 2 : 5-*dibromo*-3-*methylthiol*-p-*cresol dibromide*, $HO\cdot C_6HMeBr_2\cdot SMeBr_2$. The latter compound crystallises in stout, almost black needles and prisms, strongly resembling iodine in appearance; it sinters at 100°, and melts at 128—130°, with the evolution of bromine and hydrobromic acid. It loses bromine on exposure to air, and when treated with bromine in chloroform solution yields 2 : 3 : 5-tribromocresol.

2 : 5-*Dibromo*-3-*methylthiol*-p-*cresol*, $OH\cdot C_6HMeBr_2\cdot SMe$, prepared

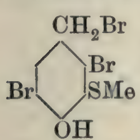
from the dibromide by shaking with aqueous sodium hydrogen sulphite, or by boiling with glacial acetic acid, forms small, compact, colourless crystals, m. p. 53—54°; from hot glacial acetic acid, it separates in colourless prisms containing acetic acid; it unites with bromine to form the original dibromide. On treatment with nitric acid in glacial acetic acid solution, it yields 2 : 5-dibromo-3-nitro-*p*-cresol.

The *acetyl* derivative of 2 : 5-dibromo-3-methylthiol-*p*-cresol crystallises in short, colourless prisms, m. p. 88—89°.

2 : 5-*Dibromo*-p-*cresol*-3-*methylsulphoxide*, $OH{\cdot}C_6HMeBr_2{\cdot}SOMe$, obtained together with the pseudo-bromide described below by shaking an ethereal solution of 2 : 5-dibromo-3-methylthiol-*p*-cresol dibromide with water, forms small, lustrous prisms, which sinter at 185°, and melt at 188—190° (decomp.); on treatment with saturated aqueous hydrobromic acid, it is reconverted into the dibromide.

2 : 5-*Dibromo*-p-*cresol*-3-*methylsulphone*, $HO{\cdot}C_6HMeBr_2{\cdot}SO_2Me$, prepared by oxidising 2 : 5-dibromo-3-methylthiol-*p*-cresol with hydrogen peroxide in glacial acetic acid solution, crystallises in lustrous needles, m. p. 160—161°.

2 : 5-*Dibromo*-3-*methylthiol*-p-*cresol* ψ-*bromide* (annexed formula) is obtained from the above-mentioned dibromide either by shaking with water in ethereal solution or by the action of glacial acetic acid and anhydrous potassium acetate; it crystallises in long, colourless needles, m. p. 130—131°, yields an orange-red *additive* product with bromine, and in contact with alkali slowly acquires a greenish colour, finally becoming almost black. On treatment with aqueous sodium acetate and ether, it is converted into an intensely black *quinone*, probably belonging to the stilbene series. F. B.



Synthesis of 4-Hydroxyphenanthrene. ROBERT BEHREND and WILHELM LUDEWIG [and, in part, THEODOR KLINCKHARD] (*Annalen*, 1911, **379**, 351—362).—4-Hydroxyphenanthrene has been synthesised by a method analogous to that for the synthesis of a 4-naphthol from phenyl*iso*crotonic acid.

Full details are given of the best method for preparing β-naphthaldehyde from calcium α-naphthoate and calcium formate, the yield being about 65% of the theoretical.

β-*Naphthylparaconic acid*, $C_{10}H_7{\cdot}CH{<}\begin{matrix}CH(CO_2H){\cdot}CH_2\\ O\text{——————}CO\end{matrix}$, obtained by heating the aldehyde with anhydrous sodium succinate (1·2 mols.) and freshly distilled acetic anhydride (1·3 mols.) at 108—114° for six to eight hours after keeping overnight in a closed vessel at the ordinary temperature, is extracted with hot carbon disulphide to remove colouring matter, dissolved in sodium hydrogen carbonate solution, precipitated with hydrochloric acid, and crystallised from hot water.

It has m. p. 169—170° (decomp.) when the bath is previously heated to 160°. When dissolved in the theoretical amount of $N/3$-potassium hydroxide solution, then well cooled, and acidified with the theoretical amount of sulphuric acid and extracted with ether, β-*naphthylitamalic acid*, $C_{10}H_7{\cdot}CH(OH){\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$, is obtained. It has m. p. 124—125° (decomp.), and is transformed readily into the paraconic acid.

*β-Naphthyl*isocrotonic *acid*, $C_{10}H_7 \cdot CH{:}CH \cdot CH_2 \cdot CO_2H$, is formed together with 4-hydroxyphenanthrene (Pschorr and Jackel, Abstr., 1900, i, 488) and naphthylbutyrolactone when the paraconic acid is heated at 200—275°, or when it is distilled slowly. The acid dissolves in dilute sodium carbonate solution, crystallises from carbon disulphide in glistening rods, or from toluene in glistening plates, m. p. 163—164°, and when heated for some time at 100° yields 4-hydroxyphenanthrene.

β-Naphthylbutyrolactone, $C_{10}H_7 \cdot CH <\begin{matrix} CH_2 \cdot CH_2 \\ O \text{——} CO \end{matrix}$, crystallises from water in small, glistening, colourless plates, m. p. 120—121°, after sintering at 115—116°. J. J. S.

Reactions which lead to the Formation of Iodine Derivatives. G. Gérard (*Chem. Zentr.*, 1910, ii, 1050; from *Bull. Sci. Pharmacol.*, 1910, **17**, 381—382).—When a solution of 2 grams of resorcinol and 1 gram of iodine in 10 grams of alcohol and 20 grams of water is mixed with a solution of 2 grams of borax and 1 gram of iodine in 10 grams of alcohol and 20 grams of water, a colourless solution is obtained which does not yield a blue coloration with starch paste; on boiling the solution, or exposing it to light, an intense red coloration is produced, and the mixture gives a reaction with starch paste. When the solution is concentrated, violet, hexagonal plates are deposited, which are soluble in water, alcohol, and ether (tri-iodoresorcinol ?). Another colourless solution, in which free iodine cannot be detected, is obtained by mixing a solution containing resorcinol, iodine, and sodium benzoate with a solution containing resorcinol, iodine, and sodium salicylate. If the resorcinol is replaced by tannin, brown solutions are obtained; these show no reactions for free iodine, and, when dried at a temperature of 50°, yield brown scales having a sweet, and not an astringent, taste. W. P. S.

Basic Properties of Oxygen: Compounds of the Halogen Acids with Benzene Derivatives Containing Oxygen. O. Maass and Douglas McIntosh (*J. Amer. Chem. Soc.*, 1911, **33**, 70—71).—Baeyer and Villiger (Abstr., 1901, i, 658) have stated that the substitution of positive groups, such as alkyl groups, for the hydrogen in water renders the oxygen basic, whilst negative groups, like phenyl, do not have this effect, and that such compounds as phenol and benzophenone do not yield salts with acids. It is now shown that this generalisation is not correct, since many substances containing the phenyl group dissolve in liquid hydrogen bromide or chloride with formation of compounds.

The following compounds have been obtained in the crystalline state: resorcinol *hydrobromide*, $C_6H_4(OH)_2,4HBr$, m. p. −71°; benzoic acid *hydrobromide*, $C_7H_6O_2,2HBr$, m. p. −44°; benzophenone *hydrobromide*, $COPh_2,6HBr$, m. p. −42°; and resorcinol *hydrochloride*, $C_6H_4(OH)_2,3(\text{or } 4)HCl$, and benzophenone *hydrochloride*,

$$(C_6H_5)_2CO,7HCl,$$

both with m. p. below −85°. The benzophenone compounds contain more acid than would unite with the oxygen if it were quadri- or even

sexa-valent, and it is therefore suggested that they should at present be regarded merely as substances with acid of crystallisation.

E. G.

Derivatives of Butyl*cyclo*hexane. GEORGES DARZENS and H. ROST (*Compt. rend.*, 1911, **152**, 607—609).—p-*tert.*-Butylphenol is readily hydrogenated by Sabatier and Senderens' method if the nickel is prepared by reduction below 260°; the yield is practically theoretical if hydrogenation is effected below 160°. tert.-*Butyl*-cyclo*hexan*-4-*ol*, $C_{10}H_{20}O$, m. p. 83°, b. p. 110—115°/15 mm., has a camphoraceous odour; on oxidation with chromic acid it yields tert.-*butyl*cyclo*hexan*-4-*one*, b. p. 106—109°/18 mm., 65—67°/3 mm.; the *semicarbazone* has m. p. 215—216°.

1-*Methyl*-3-tert.-*butyl*cyclo*hexan*-6-*one*, b. p. 118—122°/31 mm., has a fruity odour.

5-tert.-*Butyl*-m-*xylen*-2-*ol*, prepared by sulphonating butylxylene and heating the product with potassium hydroxide, has m. p. 75°, b. p. 107°/6 mm. On hydrogenation it yields 1 : 3-*dimethyl*-5-tert.-*butyl*-cyclo*hexan*-2-*ol*, a viscous liquid, b. p. 123—124°/22 mm. 1 : 3-*Dimethyl*-5-tert.-*butyl*cyclo*hexan*-2-*one* has b. p. 120—121°/21 mm., and, like the foregoing ketone, does not form a semicarbazone. W. O. W.

Crystallography of Some Organic Additive Compounds. GIOVANNI BOERIS (*Zeitsch. Kryst. Min.*, 1911, **49**, 72—73; from *Mem. R. Accad. Sci. Ist. Bologna*, 1907-1908, [vi], **5**, 303—308).—The additive compound of *iso*apiole and picryl chloride,

$$C_{12}H_{14}O_4,C_6H_2Cl(NO_2)_3,$$

forms dark garnet-red, triclinic crystals [$a:b:c = 0{\cdot}5453:1:0{\cdot}4847$; $\alpha = 86°6'$, $\beta = 111°58'$, $\gamma = 106°57'$].

The compound of *iso*apiole with *s*-trinitrotoluene,

$$C_{12}H_{14}O_4,C_6H_2Me(NO_2)_3,$$

forms scarlet, triclinic crystals [$a:b:c = 0{\cdot}5495:1:0{\cdot}4907$; $\alpha = 87°36'$, $\beta = 112°34'$, $\gamma = 105°16'$].

This and other examples not quoted confirms the author's view that the groups Cl and Me replace one another isogonically.

L. J. S.

Oxidation of Tertiary Alcohols of the Tolylallyl Series. E. GRISHKEWITSCH-TROCHIMOWSKY (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1543—1552).—The author has studied the products of oxidation of some of the alcohols previously described (Abstr., 1909, i, 151; 1910, i, 108) by means of potassium permanganate.

p-Tolylmethylallylcarbinol yields: (1) β-*p*-tolylpentane-$\beta\delta\epsilon$-triol, $C_6H_4Me{\cdot}CMe(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, needles, m. p. 101—103°, and (2) the unstable β-*p*-tolyl-β-methylhydracrylic acid, m. p. 103—106°; on dry distillation this acid yields β-*p*-tolylpropylene (compare Matschurevitsch, Abstr., 1909, i, 304).

p-Tolylethylallylcarbinol yields: (1) γ-p-*tolylhexane*-$\gamma\epsilon\zeta$-*triol*,

$$C_6H_4Me{\cdot}CEt(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH,$$

colourless needles, m. p. 89—90·5°, and (2) β-p-*tolyl*-β-*ethylhydracrylic acid*, $C_6H_4Me{\cdot}CEt(OH){\cdot}CH_2{\cdot}CO_2H$, short prisms and plates, m. p.

109—111°, decomposing at 125°; the *silver* and *barium* salts were prepared. On dry distillation, the acid yields *β*-p-*tolyl*-Δ^{α}-*butylene*, $C_6H_4Me\cdot CEt\colon CH_2$, b. p. 206—209°/750 mm., $D_4^{22\cdot5}$ 0·8926, $n_D^{22\cdot5}$ 1·52735.

p-Tolylpropylallylcarbinol gives: (1) *δ*-p-*tolylheptane-αβδ-triol*, $C_6H_4Me\cdot CPr^{\alpha}(OH)\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, a very viscous, yellow liquid, and (2) *β*-p-*tolyl-β-propylhydracrylic acid*,

$$C_6H_4Me\cdot CPr^{\alpha}(OH)\cdot CH_2\cdot CO_2H,$$

thin needles, m. p. 99—101°, of which the *barium* and *sodium* salts were prepared. On dry distillation, the acid yields *β*-p-*tolyl*-Δ^{α}-*amylene*, $C_6H_4Me\cdot CPr^{\alpha}\colon CH_2$, as a colourless liquid, b. p. 221—224°/760 mm.

p-Tolyl*iso*propylallylcarbinol yields: (1) *β-methyl-γ*-p-*tolylhexane-γεζ-triol*, $CHMe_2\cdot C(C_6H_4Me)(OH)\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, as a viscous, pale yellow liquid, and (2) *β*-p-*tolyl-β*-iso*propylhydracrylic acid*, $C_6H_4Me\cdot CPr^{\beta}(OH)\cdot CH_2\cdot CO_2H$, thin, colourless needles, m. p. 106—108°; the *potassium*, *sodium*, and *silver* salts were prepared. On dry distillation, the acid gives *β*-p-*tolyl-γ-methyl*-Δ^{α}-*butylene*, $C_6H_4Me\cdot CPr^{\beta}\colon CH_2$, as a colourless liquid, b. p. 210—212°, D_4^{27} 0·8838, n_D^{27} 1·52543. T. H. P.

Preparation of Secondary Amino-alcohols. LES ETABLISSEMENTS POULENC FRÈRES and ERNEST FOURNEAU (D.R.-P. 228205).—The preparation of numerous secondary amino-alcohols of the general formula $OR\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NR_1R_2$ (where R is an aryl or substituted aryl residue; R_1 an hydrogen, alkyl, aryl, or substituted aryl or alkylaryl group; R_2 an alkyl, aryl, or substituted aryl or alkylaryl residue) by the interaction of glycerol ethers on primary or secondary aliphatic or aromatic amines, or on amino-phenols or -naphthols, has previously been described (compare Fourneau, Abstr., 1910, i, 246, 822).

p-*Tolyl glycide ether*, $C_6H_4Me\cdot O\cdot CH_2\cdot CH{<}\genfrac{}{}{0pt}{}{CH_2}{O}$, a liquid, b. p. 165—166°/20 mm., is obtained by heating together *p*-cresol, dichlorohydrin, and sodium hydroxide (2 mols.); this when boiled during several days with dimethylamine (in petroleum solution) yields *dimethylamino*-p-*tolyloxypropanol*,

$$C_6H_4Me\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NMe_2,$$

a colourless oil, b. p. 175—176°/10 mm., and strongly alkaline to litmus; the *hydrochloride* of the *benzoyl* derivative has m. p. 155°.

The glycide ether, prepared from thymol and epichlorohydrin or dichlorohydrin, is stated to have m. p. 61° and b. p. 176°/20 mm. (Abstr., 1910, i, 246 gives 88° and 180° respectively).

Dimethylamino-β-phenoxy-α-methoxypropanol,

$$OMe\cdot C_6H_4\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NMe_2,$$

crystals, m. p. 60—61°, is prepared by the action of dimethylamine on the corresponding glycide ether (b. p. 166—168°/12 mm.); the *methiodide* has m. p. 114°.

The *glycide ether*, prepared from *β*-naphthol and dichlorohydrin, has b. p. 212—213°/12 mm., and *γ*-dimethylamino-*β*-naphthoxypropanol, b. p. 217°/16 mm. (*loc. cit.* gives 217°/11 mm.). The action of dichlorohydrin on sodium *p*-nitrophenoxide yields the glycide ether, b. p.

250—255°/15 mm., m. p. 69°, accompanied by glycerol di-*p*-nitrophenyl ether.

γ-Dimethylamino-α-phenoxypropanol has a fish-like odour, and b. p. 162°/11 mm. (*loc. cit.* gives 161°/13 mm.); its ethobromide has m. p. 110° (*loc. cit.* 112°).

γ-Anilinophenoxypropanol yields with gold chloride a violet-red precipitate, which rapidly changes to green; and with potassium mercury iodide an oily, green precipitate; the *picrate* separates as an oil, which after crystalisation from alcohol forms needles, m. p. 121—122°. F. M. G. M.

Two New Methods for Synthesising Nitriles. VICTOR GRIGNARD (*Compt. rend.*, 1911, **152**, 388—390).—Cyanogen chloride, preferably prepared by Held's method, is dried over calcium chloride and passed into dry ether at 0°. An ethereal solution of an organo-magnesium halide is now allowed to flow in drop by drop. After some hours the liquid is treated in the usual way, and a good yield (55—80%) of a pure nitrile is thus obtained. The reaction is represented as: $RMgX + CNCl = MgXCl + R\cdot CN$. The other halogen derivative of cyanogen are not suitable for this preparation; thus, with cyanogen iodide the reaction proceeds entirely according to the equation: $RMgBr + CNI = RI + MgBr\cdot CN$. In the case of cyanogen bromide, both reactions occur, the latter predominating. Benzonitrile, 1-naphthonitrile, anisonitrile, and phenylpropionitrile have been prepared by this process.

The second method consists of substituting cyanogen itself for the halogen derivative. It has been used to prepare benzonitrile, *iso*hexonitrile, and phenylbutyronitrile, but the yields are inferior to those obtained with the chloride. If the order of mixing the organo-magnesium compound with the cyanogen or its chloride is reversed, ketones are produced in the usual way. W. O. W.

3:5-Dibromoanthranilic Acid. FRITZ ULLMANN and EDUARD KOPETSCHNI (*Ber.*, 1911, **44**, 425—431).—3 : 5-Dibromo-2-aminobenzoic acid (Wheeler and Oates, Abstr., 1910, i, 481) is readily obtained by passing bromine vapour into a dilute solution of anthranilic acid in aqueous hydrochloric acid; it is converted by bromine water into tribromoaniline, and yields diazonium salts which are very stable in aqueous solution.

3 : 5-*Dibromophthalic acid*, prepared from the preceding acid by the Sandmeyer reaction, crystallises in colourless needles; when rapidly heated, it melts at 198°, and is simultaneously converted into the *anhydride*, m. p. 121·5°.

2 : 3 : 5-Tribromobenzoic acid has been obtained in colourless needles, m. p. 190° (compare Rosanoff and Prager, Abstr., 1909, ii, 32); the *methyl* ester crystallises in long, silky needles, m. p. 77°.

When boiled with aqueous potassium carbonate and copper, 2 : 3 : 5-tribromobenzoic acid is converted into 3 : 5-dibromosalicylic acid, m. p. 228° (Lellmann and Grothmann, Abstr., 1885, 265, give 223°).

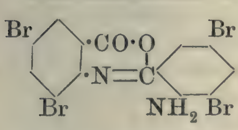
The dibromosalicylic acid obtained by Lassar-Cohn and Schultze (Abstr., 1905, i, 893), by the action of potassium hypobromite on

potassium salicylate, and considered by them to be the 5 : 6-derivative, is identical with the above-mentioned 3 : 5-dibromosalicylic acid.

4 : 6-Dibromophenylglycine-2-carboxylic acid is produced in small quantities by the interaction of 2 : 3 : 5-tribromobenzoic acid and glycine in the presence of copper. It is best prepared by brominating phenylglycine-*o*-carboxylic acid in sulphuric acid solution; it crystallises in pale yellow, microscopic needles, m. p. 248° (decomp.); the *methyl* ester has m. p. 88°.

When boiled with anhydrous potassium acetate and acetic anhydride, 4 : 6-dibromophenylglycine-2-carboxylic acid yields 5 : 7 : 5′ : 7′-tetrabromoindigotin (Grandmougin, Abstr, 1910, i, 259).

The interaction of *p*-toluenesulphonyl chloride and 3 : 5-dibromo-2-aminobenzoic acid, either in aqueous potassium carbonate or pyridine solution, leads to the formation of *dibromoanthranoyl-dibromoanthranilic acid O-anhydride* (annexed formula), which crystallises in citron-yellow needles, m. p. 342° (corr.) F. B.



Action of Nitrous Acid on Methyl Dimethylanthranilate. Josef Houben (*Ber.*, 1911, **44**, 547).—In consequence of an error in the estimation of the nitrogen, the azomethine compound obtained from methyl dimethylanthranilate has been stated to be a monomethyl derivative (this vol., i, 128). This is incorrect; the percentage of nitrogen found corresponds with the formula of a dimethyl derivative, and the condensation follows a normal course. C. S.

Turmeric Oil. III. Synthesis of γ-*p*-Tolylvaleric Acid. Hans Rupe and A. Steinbach (*Ber.*, 1911, **44**, 584—588. Compare this vol., i, 69).—Since it has been shown that curcumic acid is possibly γ-*p*-tolylvaleric acid, the synthesis of this acid has been effected; the product, however, is not curcumic acid, although very similar to it.

γ-p-*Tolyl-γ-methyl*iso*crotonic acid*, $C_6H_4Me\cdot CMe\colon CH\cdot CH_2\cdot CO_2H$, m. p. 86—87°, is obtained by adding ethereal magnesium methyl iodide to ethyl β-*p*-toluoylpropionate in ether (when the order of addition is reversed hardly any reaction occurs), and decomposing the product with water and dilute sulphuric acid at 0°. When boiled for four hours with 10% sulphuric acid, it is converted into γ-p-*tolyl-γ-valerolactone*, $C_6H_4Me\cdot CMe{<}\begin{matrix}CH_2\cdot CH_2\\ O\text{---}CO\end{matrix}$, m. p. 52°, which is reduced by boiling hydriodic acid, D 1·702, and red phosphorus to γ-p-*tolylvaleric* acid, $C_6H_4Me\cdot CHMe\cdot CH_2\cdot CH_2\cdot CO_2H$, m. p. 32°, b. p. 173—174°/9 mm. Like curcumic acid (m. p. 33—34°, b. p. 168—170°/12 mm.), this acid is extremely soluble in the usual solvents; also, its calcium salt melts in boiling water. The two acids, however, liquefy when mixed, and yield different p-*toluidides*, that from curcumic acid having m. p. 126—127°, whilst the toluidide of the synthetic acid has m. p. 77—79°; also, the two acids yield different

products by oxidation. When *p*-tolylvaleric acid is treated with 4% potassium permanganate and sodium carbonate at 0°, the chief product is the lactone mentioned above; a small amount of *p*-tolylmethyl ketone (identified as the semicarbazide) and a *substance*, m. p. 150—151° (not identical with the acid, m. p. 150—151°, obtained amongst the products of oxidation of curcumic acid) are also formed. This result is important, since it proves that curcumic acid must have a constitution which does not admit of the formation of a lactone when the acid is oxidised. C. S.

Condensation of β-Naphthaldehyde with Methylsuccinic Acid. ROBERT BEHREND and THEODOR KLINCKHARD (*Annalen*, 1911, **379**, 362—376).—According to Fittig and Liebmann (Abstr., 1890, 775), two structurally isomeric phenyl-α-methylparaconic acids are obtained by the condensation of benzaldehyde with sodium methylsuccinate and acetic anhydride, and the two acids yield α-methylphenyl*iso*crotonic acid and the isomeric β-methyl derivative when distilled. Heptaldehyde (Fittig and Riechelmann, Abstr., 1890, 593) and valeraldehyde (Fittig and Feist, *ibid.*, 591) each yield two structurally isomeric paraconic acids when condensed with methylsuccinic acid. When β-naphthaldehyde is used, it is shown that two isomeric β-naphthylmethylparaconic acids are formed, but these are stereoisomeric, as they yield the same naphthyl-β-methyl*iso*crotonic acid when distilled. The constitution of the condensation products follows from the fact that the hydroxymethylphenanthrene obtained by the removal of water from the *iso*crotonic acid yields on distillation with zinc dust a methylphenanthrene which is not identical with Pschorr and Quade's 3-methylphenanthrene (Abstr., 1906, i, 848).

The separation of the two naphthylmethylparaconic acids can be effected by fractional crystallisation from dilute alcohol. The one acid, $C_6H_{14}O_4,H_2O$, separates from 60% alcohol in transparent, monoclinic crystals, and when slowly heated has m. p. 199—200° (decomp.), after sintering at 198—199°. The anhydrous compound has the same m. p. The *stereoisomeride*, $C_{16}H_{14}O_4$ crystallises from 50% alcohol in nodular masses of minute plates, or in well developed prisms, m. p. 174—175° (decomp.). When distilled slowly under reduced pressure, the two acids yield *naphthyl-β-methyl*iso*crotonic acid*, together with 4-hydroxy-2-methylphenanthrene, naphthyl*iso*butylene, and unaltered acid. The unsaturated acid can be separated from unaltered paraconic acids by extraction with cold carbon disulphide, and crystallises from the solvent in rectangular plates, m. p. 137—138°.

4-*Hydroxy-2-methylphenanthrene*, $C_{15}H_{12}O$, crystallises from dilute alcohol, and its alcoholic solution gives an orange-red coloration with ferric chloride and a lemon-yellow with bleaching powder solution. Its *acetyl* derivative, $C_{17}H_{14}O_2$, crystallises from dilute alcohol in slender needles or glistening plates, m. p. 110·5—111·5°. 2-*Methylphenanthrene*, $C_{15}H_{12}$, has m. p. 52—53°, and when mixed with the isomeric 3-methyl derivative has m. p. 40—42°.

*β-Naphthyl*iso*butylene*, $C_{10}H_7\cdot CH:CMe_2$, is a colourless oil, with b. p. 287—288°. J. J. S.

Chemical Investigation of Resin from the Pine (Picea excelsa). II. Lævo-pimaric Acid. JOHN KÖHLER (*Arkiv. Kem. Min. Geol.*, 1911, 4, No. 5, 1—29. Compare Abstr., 1906, i, 92, 100; 1907, i, 213).—Hitherto, the only source of pimaric acid has been galipot resin; it has now been found to occur universally in pines from Rottanne (*Picea excelsa*), usually accompanied by weaker lævo-rotatory, more easily soluble, and easily oxidisable acids, probably sapinic acids [?]. A very pure specimen was found in the winter-resin from the upper half of the trunk of one of the pines, and after recrystallisation from methyl alcohol it gave $[\alpha]_D^{20} = -280\cdot5°$, which is a higher rotation than has hitherto been found. Analysis and determination of the molecular weight by titration with alkali confirm the formula $C_{20}H_{30}O_2$. It does not possess a definite melting point, since at the melting-point temperature it undergoes a partial change into colophonic acids, the amount of change depending on the rapidity of heating. The crystals have the axial ratio:

$$[a:b:c = 0\cdot80975:1:0\cdot6102].$$

On being heated, *l*-pimaric acid changes into a mixture of an inactive colophonic acid and lævo-rotatory colophonic acids, which are identical with the α-colophonic acids prepared from sapinic acids [?].

The active colophonic acids crystallise in the monoclinic system, and are completely isomorphous with each other, so that it is not possible, with certainty, to isolate any given acid by fractional crystallisation. Inactive colophonic acid, like *l*-pimaric acid, crystallises in the rhombic system, although it is not isomorphous with it $[a:b:c = 0\cdot47698:1:\infty c]$.

Analysis of a colophonic acid with $[\alpha]_D^{20} = -83\cdot3°$, and determination of the molecular weight by titration with alkali, gave results agreeing with the formula $C_{20}H_{30}O_2$.

The colophonic acids possess the general property of forming a gel when their solutions in alcohol and ammonia are diluted with water; in this way, they may be distinguished from the naturally occurring resin acids. They are a general transformation product of the action of heat on the naturally occurring acids, such as *l*-pimaric acid and the sapinic acids.

The following classification is given:

A. Natural Resin Acids.—(1) Acids which do not oxidise in the air, and are relatively stable on heating. (2) Acids which readily oxidise in the air, and are very sensitive towards heat. Class (1) includes the pimaric acids, and class (2) the sapinic acids. On heating, both classes change into:

B. Colophonic Acids.—(1) α-Colophonic acids, lævorotatory. (2) β-Colophonic acids, dextrorotatory. Both the α- and β-acids are readily oxidised in the air, and, on heating, change into acids in the same group. (3) Inactive colophonic acids. T. S. P.

Conversion of Stable Stereoisomerides into Labile Modifications by Ultra-violet Light. II. RICHARD STOERMER [with EGON FRIDERICI, BRÄUTIGAM, and W. NECKEL] (*Ber.*, 1911, 44, 637—668. Compare Abstr., 1910, i, 114).—The stable, less fusible forms of the following compounds are transformed into the labile,

more fusible stereoisomerides when their benzene or alcoholic solutions are exposed to the action of the ultra-violet rays from a uviol lamp for several days: coumaric acid, 75; methylcoumaric acid, 75; ethylcoumaric acid, over 90; propylcoumaric acid, 85; methylcoumaramide, 50; ethylcoumaramide, 100; propylcoumaramide, 95; methyl coumarate $\longrightarrow$ coumarin; acetylcoumaric acid, over 90; methyl benzoylcoumarate; methyl a-*o*-nitro-*o'*-methoxycinnamate, 80; a-*o*-nitro-*o'*-methoxycoumaric acid, 40; *p*-methoxycinnamic acid, 25; sodium *o*-chlorocinnamate, 10; piperonylacrylic acid, 17; maleic acid; bromofumaric acid, 50; *o*-anisylcinnamic acid, 35—40; *o*-anisylcinnamide, 70; *o*-anisylcinnam-methylamide, 36, and corresponding ethylamide, 40; b-*o*-anisyl-*α*-methylcinnamic acid, 5, and the corresponding amide, 5; cinnamic $\longrightarrow$ *iso*cinnamic acid, m. p. 42°, 30—40; phenyl tolyl ketoxime, 40; phenyl anisyl ketoxime. In most cases the reaction is a balanced one, and the number given for each compound represents the percentage of the less fusible compound which has been transformed when equilibrium is established. Crotonic acid is not transformed to any appreciable extent.

The method is recommended as a suitable one for the preparation of *allo*-stereoisomerides in several cases, and also for the detection of spatial isomerism between a pair of compounds. In a few instances the addition of methyl or ethyl alcohol to the unsaturated compound occurs during the exposure to the ultra-violet light, but the amounts of such products are usually small. It is suggested that the transformation and the percentage amount transformed depends on the energy differences between the stereoisomerides. Sodium fumarate is not transformed, although the corresponding acid yields 30% of maleic acid.

The following new compounds are described: *propylcoumaric* [a-o-*propoxycinnamic*] *acid*, $OPr\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$, obtained by hydrolysing the corresponding methyl ester, crystallises from dilute alcohol in glistening needles, m. p. 104—105°, and the stereoisomeric *propylcoumarinic* [b-o-*propoxycinnamic*] *acid* has m. p. 83—84°. The solubilities of the two acids in light petroleum at 18° are 0·106 and 0·301% respectively. Both compounds with sodium amalgam yield b-*propoxyphenylpropionic acid*, $OPr\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO_2H$, m. p. 63°.

b-o-*Methoxycinnamamide* can be obtained by the action of phosphorus pentachloride on a dry ethereal solution of b-*o*-methoxycinnamic acid (compare Perkin, Trans., 1877, 31, 422) and treating the product with ice-cold ammonium hydroxide solution; it crystallises from carbon disulphide in needles, m. p. 62·5—63·5°. a-o-*Ethoxycinnamamide*, $C_{11}H_{13}O_2N$, has m. p. 161°, and the stereoisomeric b-o-*ethoxycinnamamide*, m. p. 115—116°.

a-o-*Propoxycinnamamide*, $C_{12}H_{15}O_2N$, has m. p. 145°, and *β*-o-*propoxycinnamamide*, m. p. 104°. b-o-*Acetoxycinnamamic acid*, $OAc\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$, prepared by the action of acetic anhydride on dry sodium *β*-coumarate at 0°, crystallises from carbon disulphide, has m. p. 85°, and when boiled with water for some time yields coumarin. b-o-*Benzoyloxycinnamic acid*, $C_{16}H_{12}O_4$, forms compact crystals from carbon disulphide, and has m. p. 96—97°. *Methyl* a-o-*benzoyloxycinnamate*, $C_{17}H_{14}O_4$, obtained by benzoylating

methyl coumarate, crystallises from alcohol in slender needles, m. p. 87°, and on hydrolysis yields benzoic and coumaric acids.

Methyl b-o-*benzoyloxycinnamate*, prepared from the silver salt of the corresponding acid, has m. p. 46°. *Ethyl* b-o-*methyloxycinnamate*, obtained from the sodium salt and ethyl sulphate, has b. p. 291—292·5°, and the isomeric *methyl* b-o-*ethyloxycinnamate*, b. p. 288·5—289·5°; each ester gives the corresponding acid on hydrolysis, and this points to the conclusion that β-coumaric acid cannot have the dihydroxylic structure, $C_6H_4<\begin{matrix}O—C(OH)_2\\ CH:CH\end{matrix}$, as the two esters should then be identical. p-*Methoxy*allo*cinnamic acid*, $C_{10}H_{10}O_3$, separates from light petroleum in triclinic crystals, m. p. 64—65°. Its solubility in benzene at 18° is 34%, and in light petroleum, 0·28%. It does not show the properties of a crystalline liquid, and is readily transformed into the less fusible stereoisomeride when its carbon disulphide solution is mixed with a little bromine and exposed to sunlight. The *aniline* salt, $C_{26}H_{27}O_6N$, crystallises from benzene in slender needles, m. p. 68°; the *amide*, prepared by the action of phosphorus pentachloride on the acid in presence of ether and treatment of the product with ammonium hydroxide, has m. p. 129°; in the absence of ether the amide of *p*-methoxycinnamic acid (m. p. 186°) is formed.

o-*Chloro*allo*cinnamic acid*, $C_9H_7O_2Cl$, crystallises from water, and has m. p. 127°. Its solubility in benzene at 18° is 1·88%. *o*-Chlorocinnamic acid has m. p. 205° (Gabriel and Herzberg, Abstr., 1883, 1123, give 200°), and its solubility in benzene is 0·04%. When this acid or its sodium salt is exposed to ultra-violet light, it is partly transformed into the *allo*-acid, but when glacial acetic acid solutions are used, part of the acid combines with acetic acid, giving a product, $C_{11}H_{11}O_4Cl$, m. p. 212—213°. The *aniline* salt of the *allo*-acid forms slender needles, m. p. 136°; the *amide*, C_9H_8ONCl, which crystallises from dilute alcohol in blue, fluorescent needles, has m. p. 112°, and the isomeric *amide* has m. p. 163—163·5°. allo-*Piperonylacrylic acid*, $C_{10}H_8O_4$, crystallises from water, and has m. p. 96—97°. Its solubility in benzene at 18° is 5·9%. Its *aniline* salt has m. p. 83·5—84°; the *amide*, $C_{10}H_9O_3N$, crystallises from ether in glistening plates, m. p. 131°, and the isomeric *amide* from alcohol in slender needles, m. p. 180°.

The piperidine salt of *o*-anisylcinnamic acid has m. p. 145°, not 54—55°, and the silver salts of both isomeric acids are soluble in benzene. o-*Anisylcinnamamide*, $C_{16}H_{15}O_2N$, has m. p. 137°, and its solubility in benzene is 0·8%; the *stereoisomeride* has m. p. 115—116°, and its solubility in benzene is 1·7%. o-*Anisylcinnam-methylamide*, $C_{17}H_{17}O_2N$, has m. p. 121°; the corresponding *ethylamide*, $C_{18}H_{19}O_2N$, m. p. 101°, and the respective stereoisomerides, m. p.'s 104—105° and 74—80°. o-*Anisylcinnambenzylamide* has m. p. 144—145°; the *amylamide*, m. p. 102—103°, and the *anilide*, m. p. 138°.

The β-anisyl-α-methylcinnamic acids are most readily prepared from *o*-methoxybenzophenone and methyl α-bromopropionate; the condensation product, *methyl* β-*phenyl*-β-*anisyl*-α-*methylhydracrylate*, $C_{18}H_{20}O_4$,

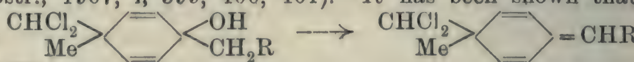
crystallises from alcohol in brilliant, rhombic crystals, m. p. 82—83°, and when treated with dry hydrogen chloride in methyl-alcoholic solution containing sodium sulphate yields methyl β-anisyl-α-methylcinnamate, m. p. 60—61°, together with the *allo*-ester.

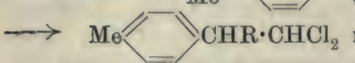
The solubilities of the two acids in benzene are 11·6 and 20·2%, and the *amides*, $C_{17}H_{17}O_2N$, of the two acids melt at 137—138° and 115—118° respectively.

The conversion of b-*o*-ethoxycinnamic acid in carbon disulphide solution by means of iodine (compare Michael and Lamb, Abstr., 1907, i, 134) depends on the concentration of the iodine solution.

It is shown that the methoxy-groups in the methyl ether of *o*-nitrosalicylic acid and in *m*-nitro-*o*-methoxybenzaldehyde are readily hydrolysed when boiled with sodium carbonate solution. *m*-Nitro-*o*-methoxybenzoic acid has m. p. 194° (compare Keller, Abstr., 1908, i, 285).

When a solution of mesaconic acid is subjected to the action of ultra-violet light, water or methyl alcohol appears to combine with the acid. J. J. S.

Hydroaromatic Compounds. Carboxylic Acid of the "Semibenzene" Group. KARL AUWERS (*Ber.*, 1911, **44**, 588—601. Compare Abstr., 1907, i, 399, 400, 401).—It has been shown that the changes: 

 readily occur when R is hydrogen or an alkyl group. The present communication shows that R may also be a carboxyl group.

Ethyl 4-*hydroxy*-1-*methyl*-1-*dichloromethyl*cyclo*hexadiene*-4-*acetate* (I) $CO_2Et{\cdot}CH_2{\cdot}C(OH){<}{}^{CH:CH}_{CH:CH}{>}CMe{\cdot}CHCl_2$, is obtained in an impure state as a viscous, yellow oil by heating a benzene solution of 4-keto-1-methyl-1-dichloromethyl*cyclo*hexadiene with ethyl bromoacetate and zinc, and decomposing the product with dilute sulphuric acid. The ester cannot be purified, owing to its tendency to lose the elements of water, but by the careful hydrolysis of its concentrated alcoholic solution by potassium hydroxide at 0° it yields the corresponding *acid*, $C_{10}H_{12}O_3Cl_2$, m. p. 119° (which cannot be kept long), and the dehydrated derivative thereof, 1-*methyl*-1-*dichloromethyl*cyclo*hexadiene*-Δ^4-*acetic acid* (II), $CO_2H{\cdot}CH{:}C{<}{}^{CH:CH}_{CH:CH}{>}CMe{\cdot}CHCl_2$, m. p. 107—108°, the two acids being separated by the greater solubility of the latter in benzene. The *ethyl* ester of the latter acid can be obtained by treating the preceding ester (I) with 98% formic acid, or in a pure state from the silver salt of the acid (II) and ethyl iodide. It has $D_4^{21\cdot9}$ 1·2151, n_D 1·56911, and the presence of three conjugated double linkings is denoted by the exaltations of the specific and molecular refractions and the dispersion. By treatment with concentrated sulphuric acid at 0° for eighteen hours, the ester is converted into *ethyl* 4-*aldehydo*-2 (or 3)-*methylphenylacetate*, $CHO{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}CO_2Et$, b. p. 160—172°/13 mm., which is isolated as the *semicarbazone*, $C_{13}H_{17}O_3N_3$,

m. p. 191—192° (compare Abstr., 1907, i, 399); the *semicarbazone* of the free acid has m. p. 234—235°.

1-Methyl-1-dichloromethyl*cyclo*hexadiene-Δ^4-acetic acid (II) can also be obtained by the hydrolysis of its ester by 50% alcoholic potassium hydroxide in the cold, or by treating 4-hydroxy-1-methyl-1-dichloromethyl*cyclo*hexadiene-4-acetic acid with 98% formic acid; in the latter method 1-methyl-4-$\beta\beta$-dichloroethylbenzene (IV) (Abstr., 1907, i, 400) is obtained as a by-product by the elimination of carbon dioxide and simultaneous intramolecular change of the "semibenzene" acid (II).

Ethyl $\beta\beta$-*dichloro*-α-p-*tolylpropionate*, $C_6H_4Me\cdot CH(CHCl_2)\cdot CO_2Et$, b. p. 162—164°/15 mm., $D_4^{19\cdot4}$ 1·2011, n_D 1·52137, is obtained by heating the ester (I) or, in a purer state, the ester of II; its aromatic character is proved by the very small exaltations of its molecular refraction and dispersion. By hydrolysis with alkalis, the ester yields either a mixture of the acid and β-chloro-α-p-tolylacrylic acid or the latter alone. $\beta\beta$-*Dichloro*-α-p-*tolylpropionic acid*, $C_{10}H_{10}O_2Cl_2$, m. p. 156°, therefore, is best obtained by heating the "semibenzene" acid (II) on the water-bath; when heated over a naked flame, the acid II yields a considerable quantity of 1-methyl-4-$\beta\beta$-dichloroethylbenzene (IV). $\beta\beta$-Dichloro-α-p-tolylpropionic acid can be titrated with sodium hydroxide, but is much more sensitive to the attack of an excess of the alkali than the isomeric acid (II); for whilst the latter can be warmed with 10% sodium hydroxide without decomposition, the former is converted into β-*chloro*-α-p-*tolylacrylic acid*, $CHCl:C(C_6H_4Me)\cdot CO_2H$, m. p. 112°. This acid is obtained from each of the preceding compounds—most conveniently from the ester (I)—by heating with aqueous or alcoholic alkalis. It forms an *ethyl* ester, $C_{12}H_{13}O_2Cl$, b. p. 155—156°/15 mm., $D_4^{20\cdot9}$ 1·1353, n_D 1·53579, which is oxidised in aqueous acetone by potassium permanganate, yielding ethyl p-tolylglyoxylate.

Unsuccessful attempts have been made to obtain compounds similar to the preceding from 2-keto-1-methyl-1-dichloromethyl*cyclo*hexadiene and 2-keto-1 : 5-dimethyl-1-dichloromethyl*cyclo*hexadiene. C. S.

Action of Ethyl Chlorocarbonate on Sodium Derivatives of Ketones Prepared by means of Sodamide ALBIN HALLER and ÉDOUARD BAUER (*Compt. rend.*, 1911, 152, 551—558).—The sodium derivatives of aliphatic or mixed aromatic-aliphatic ketones of the type $R\cdot CO\cdot CHR'R''$, on treatment with ethyl chlorocarbonate in benzene solution, form carbonates of the type $CR'R'':CR\cdot O\cdot CO_2Et$. Under the same conditions, however, ketones of the type

$$CPh\cdot CO\cdot CH_2R$$

yield compounds having the constitution $CO_2Et\cdot CR:CPh\cdot O\cdot CO_2Et$. On hydrolysis with alcoholic sodium hydroxide these form sodium ethyl carbonate and monoalkyl derivatives of ethyl benzoylacetate; the latter are thus obtained in a purer condition than when prepared by direct alkylation of the ester.

The sodium derivative of phenyl *iso*propyl ketone reacts vigorously with ethyl chlorocarbonate, giving a 70% yield of α-*ethylcarbonato*-α-*phenyl*-Δ^α-iso*butylene*, $CMe_2:CPh\cdot O\cdot CO_2Et$, m. p. 41—42°. The constitution of this compound follows from its conversion into sodium

ethyl carbonate and phenyl *iso*propyl ketone when treated with the calculated amount of water and sodium ethoxide. It is the enolic form of *ethyl benzoyl*iso*butyrate*, $COPh \cdot CMe_2 \cdot CO_2Et$, a liquid of b. p. 145—146°/13 mm. : also obtained by the action of methyl iodide and sodium ethoxide on Perkin and Colman's ethyl methylbenzoylacetate (Trans., 1886, **49**, 156); the *oxime* has m. p. 135—136°.

Propiophenone gives rise to *α-ethylcarbonato-α-phenyl-Δ^α-propylene*, $CHMe\colon CPh \cdot O \cdot CO_2Et$, b. p. 140—145°/11—12 mm., together with *ethyl β-ethylcarbonato-α-methylcinnamate*, $CO_2Et \cdot O \cdot CPh\colon CMe \cdot CO_2Et$, b. p. 182—185°/11—12 mm.

Butyrophenone gives *α-ethylcarbonato-α-phenyl-Δ^α-butylene*,

$$CHEt\colon CPh \cdot O \cdot CO_2Et,$$

b. p. 143°/10 mm., and *ethyl β-ethylcarbonato-α-ethylcinnamate*,

$$CO_2Et \cdot O \cdot CPh\colon CEt \cdot CO_2Et,$$

m. p. about 35°, b. p. 183—184°/10 mm.

Acetophenone in the same way gives diethyl benzoylmalonate, together with an oil containing (1) a *compound*, $C_{11}H_{14}O_4$, b. p. 128—129°/11 mm.; it forms an unstable *bromo*-derivative, m. p. 78°; (2) ethyl β-carbethoxycinnamate.

Pentamethylacetone forms *γ-ethylcarbonato-βδδ-trimethyl-Δ^β-pentene*, $CMe_2\colon C(O \cdot CO_2Et) \cdot CMe_3$, b. p. 89—90°/13·5 mm.

*cyclo*Hexanone yields an oil containing (1) a substance, b. p. 108—110°/20 mm., having the composition of ethyl *cyclo*hexanone-carboxylate; (2) Wallach's di*cyclo*hexanone, characterised by the oxime, m. p. 155°, and the *semicarbazone*, m. p. 210—212°; (3) *ethyl-carbonato-Δ¹-*cyclo*hexene*, $C_6H_9 \cdot O \cdot CO_2Et$, b. p. 108—110°/20 mm., an enolic form of the ester of Gardner, Perkin, and Watson's *cyclo*hexanone-2-carboxylic acid (Trans., 1910, **97**, 1796). W. O. W.

Phenolphthalein and its Colourless Salts. PHILIP A. KOBER and J. THEODORE MARSHALL (*J. Amer. Chem. Soc.*, 1911, **33**, 59—70).—During the course of certain work on tests for blood (Kober, Lyle, and Marshall, Abstr., 1910, ii, 910) it was observed that the colour of a standard solution of phenolphthalein gradually faded. Although this phenomenon has been observed by others, it has not hitherto been fully investigated, and the present work was therefore undertaken.

The rate of fading has been determined colorimetrically, and a curve has been obtained which resembles that of an irreversible unimolecular reaction. It has been shown by conductivity measurements that the change of colour is due to a chemical reaction in which alkali hydroxide takes part. From a study of concentrations at equilibrium, it has been found that the intensity of the colour depends on two factors: (1) dissociation or hydrolysis of the coloured dibasic salt, and (2) hydration with the formation of a colourless tribasic salt (compare Meyer and Hantzsch, Abstr., 1907, i, 932). If follows therefore that phenolphthalein is not an accurate colorimetric standard.

The *tripotassium* salt, $\genfrac{}{}{0pt}{}{CO_2K \cdot C_6H_4}{OK \cdot C_6H_4} > C < \genfrac{}{}{0pt}{}{C_6H_4 \cdot OK}{OH}, 5H_2O$, has been isolated; it forms colourless, microscopic plates, and is fairly stable; when, however, an aqueous solution is boiled or left for a consider-

able time, it develops an intense red colour. The corresponding *trisodium* salt crystallises in cubes.

When the tripotassium salt is administered hypodermically to dogs, it produces a purgative effect. E. G.

Phenolphthalein Derivatives and their Behaviour as Indicators. Erwin Rupp (*Arch. Pharm.*, 1911, **249**, 56—68).—The behaviour of phenolphthalein derivatives containing negative substituents towards ammonia and alkaloids indicates that this is better explained by the chromophore theory of indicators than by the dissociation theory.

Tetrabromophenolphthalein, $C_6Br_4<^{-O-}_{CO}>C(C_6H_4\cdot OH)_2$, m.p. 280—285° (decomp.), prepared by heating tetrabromophthalic anhydride with phenol in sulphuric acid, crystallises from warm alcohol or acetic acid, and gives a violet colour with alkalis, which is discharged by acids. When heated with bromine in acetic acid, it gives *octabromophenolphthalein*, $C_6Br_4<^{-O-}_{CO}>C(C_6H_2Br_2\cdot OH)_2$, which crystallises in colourless needles, and gives a blue colour with alkalis.

Tetraiodophenolphthalein was not obtained crystalline; it gives a violet coloration, with alkalis and on heating with bromine in acetic acid gives *tetrabromotetraiodophenolphthalein*,

$$C_6I_4<^{-O-}_{CO}>C(C_6H_2Br_2\cdot OH)_2,$$

which crystallises from dilute alcohol and gives a bluish-green coloration with alkalis.

These and other halogenated phenolphthaleins, as well as nitrophenolphthalein and dibromodinitrophenolphthalein, were tried as indicators with ammonia and morphine, and the results are tabulated in detail in the original. They show that the mere acidification of the phenolphthalein molecule by the introduction of negative groups does not effect any marked improvement in the values of the phthaleins as indicators for weak bases. The introduction of negative substituents in the phenol nucleus leads to a diffuse, gradual colour change, whilst their introduction into the phthalein nucleus gives rise to a rapid colour change with bases. This is best explained on the assumption that the free phenolphthaleins exist in the *pseudo*-form and their salts in the *quinonoid* form. The value of any phthalein as an indicator depends on the rapidity with which this change may occur, and this is influenced by the position of the substituents. This view is supported by the fact that acylated phenolphthaleins are unsuitable for use as indicators. T. A. H.

Acylated Salicylosalicylic [*o*-2-Acyloxybenzoyloxybenzoic] Acids. Alfred Einhorn [with Gustav Haas, Alexander von Bagh, Carl Ladisch, and Leo Rothlauf] (*Ber.*, 1911, **44**, 431—439).—In the preparation of *o*-ethylcarbonatobenzoic acid by the interaction of ethyl chlorocarbonate and salicylic acid in pyridine solution, *o*-2-ethylcarbonatobenzoyloxybenzoic acid is produced simultaneously. The relative proportions of the two acids depend on the time the reaction

is allowed to proceed, the last-mentioned acid being produced in larger quantity the longer the reaction mixture is kept.

o-2-*Ethylcarbonatobenzoyloxybenzoic acid*,

$$CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

crystallises from benzene in small, white needles, m. p. 119°. It dissolves in strong aqueous ammonia with a yellow colour, and at the same time is converted into salicylic acid and salicylamide. When hydrolysed with dilute ammonia according to Fischer's method, or when heated with aluminium bromide in benzene solution, it yields *o*-salicyloxybenzoic acid, $OH\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$ (Abstr., 1909, i, 803). It has also been obtained (1) by the action of ethyl chlorocarbonate on salicylic acid in benzene solution in the presence of dimethylaniline, (2) by the action of ethyl *o*-ethylcarbonatobenzoylcarbonate, $CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot CO_2Et$, on salicylic acid in dimethylaniline or pyridine solution, and (3) by the interaction of ethyl chlorocarbonate ($\frac{3}{4}$ mol.) and sodium salicylate (1 mol.) in acetone solution. When excess of ethyl chlorocarbonate is employed in the latter reaction, the main product is *o*-ethylcarbonatobenzoic acid, which forms leafy crystals, m. p. 95°; from carbon tetrachloride it separates in pearly leaflets of the composition $2CO_2Et\cdot O\cdot C_6H_4\cdot CO_2H,CCl_4$; these rapidly lose carbon tetrachloride on being exposed to the air.

o-2-*Methylcarbonatobenzoyloxybenzoic acid*,

$$CO_2Me\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

prepared by the action of methyl chlorocarbonate on salicylic acid in pyridine solution, crystallises in clusters of tapering needles, m. p. 112°.

o-2-*Acetoxybenzoyloxybenzoic* (*acetylsalicylosalicylic*) *acid*,

$$OAc\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

prepared by the prolonged action of pyridine on ethyl *o*-acetoxybenzoylcarbonate, crystallises in leaflets, m. p. 161—162° (compare Einhorn and Seuffert, this vol., i, 53). It has also been obtained (1) by the action of ethyl *o*-acetoxybenzoylcarbonate on salicylic acid in the presence of dimethylaniline, and on sodium salicylate in dilute alcoholic or acetone solution, (2) by the interaction of pyridine and *o*-acetoxybenzoic anhydride, and (3) by the action of *o*-acetoxybenzoic anhydride on salicylic acid in the presence of pyridine, or on sodium salicylate in acetone solution. F. B.

Ketones Derived from Phenylpropionic Acid. JEAN B. SENDERENS (*Compt. rend.*, 1911, **152**, 384—386. Compare Abstr., 1909, i, 286, 627; 1910, i, 11, 179, 318, 489; this vol., i, 134).— When a mixture of phenylpropionic acid (1 mol.) and an aliphatic acid (3 mols.) are passed over thorium oxide at about 460°, the product consists almost exclusively of the mixed aromatic ketone and the symmetrical aliphatic ketone. The following compounds, prepared by this method, are liquids with an agreeable odour; except in the first case their oximes are oily.

α-Phenylbutan-γ-one, b. p. 228·5°/750 mm. (corr.), D_4^0 0·9877; the *oxime*, m. p. 80°; the *semicarbazone*, m. p. 136°. *α-Phenylpentan-γ-one*, $CH_2Ph\cdot CH_2\cdot COEt$, b. p. 244°/750 mm. (corr.), D_4^0 0·9793; the *semicarbazone*, m. p. 82°. *α-Phenylhexan-γ-one*, $C_{12}H_{16}O$, b. p. 263°/

760 mm. (corr.), D_4^0 0·9719. *a-Phenyl-δ-methylpentan-γ-one*, $C_{12}H_{16}O$, b. p. 256°/760 mm. (corr.), D_4^0 0·9755; the *semicarbazone*, m. p. 86°. *a-Phenyl-ε-methylhexan-γ-one*, $C_{13}H_{18}O$, b. p. 268·5°/760 mm. (corr.), D_4^0 0·9619.

aε-Diphenylpentan-γ-one, $CH_2Ph·CH_2·CO·CH_2·CH_2Ph$, produced in small quantity during the preparation of the foregoing ketones, is best prepared by passing phenylpropionic acid over thorium oxide at about 440°. It has b. p. 347·5°/760 mm. (corr.), D_4^0 1·0356; the *semicarbazone* has m. p. 105°.

Attempts to prepare unsaturated ketones by the catalytic method have not been successful. Cinnamic acid, for example, yields metastyrene as the chief product, whilst crotonic acid furnishes only decomposition products. W. O. W.

Desmotropism of Formyldeoxybenzoin. WILHELM WISLICENUS and ALEXANDER RUTHING (*Annalen*, 1911, 379, 229—261).—It is shown that Claisen and Meyerowitz's formyldeoxybenzoin (Abstr., 1890, 359) exists in two isomeric modifications, which are represented by the two formulæ: α = COPh·CPh:CH·OH, and

β = CHO·CPh:CPh·OH.

A 60—70% yield of the formyl derivative can be obtained by the action of deoxybenzoin on a mixture of sodium ethoxide and ethyl formate under specific conditions. The crude product obtained by the addition of dilute sulphuric acid to the alkaline solution is partly molten at 75°, but resolidifies, and then has m. p. 110°. α-Formyldeoxybenzoin (hydroxymethylenedeoxybenzoin) crystallises from light petroleum (b. p. 100—120°) in sulphur-yellow needles or prisms; it is partly molten at 76—80°, but is quickly transformed into the β-isomeride. It has b. p. 183°/14 mm. It can be kept for a few days at the ordinary temperature, but is stable at temperatures above 110°. The α-compound is more soluble than the β-isomeride in most solvents, and the solutions have a yellow colour. In benzene solutions a portion of the β-compound is transformed into the α, so that an equilibrium mixture is formed, whereas alcohol readily transforms the α- into the β-isomeride, even when the greater portion of the compound is not dissolved. The α-compound is partly transformed into the β- by dissolving in benzene and alcohol, and an equilibrium mixture is obtained.

β-Formyldeoxybenzoin crystallises from alcohol in colourless, microscopic plates, m. p. 112—113°, and the fused mass, when cooled rapidly, yields crystals of the α-isomeride. Both compounds give colorations with ferric chloride; in the case of the α-compound this is best shown by using benzene solutions of the compound and of ferric chloride.

The enol-ketonic structure is ascribed to the α-compound, on account of its yellow colour and similarity to benzoin; the aldo-enolic formula is given to the β-isomeride, as it gives a coloration with Schiff's reagent (decolorised magenta). Both compounds form salts, but it is probable that during salt formation the β-compound undergoes molecular rearrangement, and all the salts obtained appear to belong to the α-series, although the product obtained by acidifying the solution of

the salts may be the α- or β-compound, according to the conditions of the experiment. The β-compound can be transformed into the α- by dissolving in alcohol containing the theoretical amount of sodium ethoxide, keeping for twelve hours, and then diluting with water and precipitating by adding sulphuric acid (dil.) drop by drop. The *copper* derivative, $(C_{15}H_{11}O_2)_2Cu$, crystallises in green plates, and has m. p. 220—221°.

When a dilute alcoholic solution of the β-compound is kept for some time, a slow change takes place; at the end of two days the solution no longer yields a copper derivative, and gives only a faint coloration with ferric chloride. This is probably due to the formation of a third isomeric form, namely, a γ-form, which is regarded as the aldo-keto-compound, O:CH·CHPh·COPh. The transformation of the β- into the γ-compound takes place more readily in methyl-alcoholic solution. The γ-compound does not form a copper derivative, and does not give colorations with ferric chloride, but reacts readily with Schiff's reagent. It has not been found possible to isolate the solid γ-compound, as on concentrating its solutions it passes over into the β- and possibly α-compounds.

The α- and β-forms yield identical derivatives, although the rates at which they react are different. Both yield an additive *compound* with ammonia, $C_{15}H_{15}ON_2$, in the form of a colourless solid, m. p. 161°, after sintering at 154°. The compound with aniline,

COPh·CPh:CH·NHPh,

crystallises from alcohol, has m. p. 92—93°, does not give a coloration with ferric chloride, but forms a yellowish-brown *copper* derivative, $(C_{21}H_{16}ON)_2Cu$, m. p. 213—214°.

Hydrazine hydrate reacts with the α-compound, yielding Curtius and Blumer's bisphenylbenzylazimethylene (Abstr., 1895, i, 608). When an alcoholic solution of hydrazine hydrate is used, the product is 3 : 4-*diphenylpyrazole*, $\begin{matrix}\text{CH}=\!=\!=\text{N}\\ \text{CHPh·CPh}\end{matrix}\!\!>\!\text{N}$, in the form of yellow needles, m. p. 154—155°. The corresponding 1 : 4 : 5-*triphenylpyrazole*,

$C_{21}H_{16}N$,

m. p. 210—211°, is formed when phenylhydrazine is used. 4 : 5-*Diphenyl*-1-p-*bromophenylpyrazole*, $C_6H_4Br\cdot N\!<\!\begin{matrix}\text{CPh:CPh}\\ \text{N}=\!=\text{CH}\end{matrix}$, crystallises in colourless, felted needles, m. p. 182—183°.

Formyldeoxybenzoin reacts with an aqueous alcoholic solution of benzenediazonium chloride and sodium acetate, yielding benzil monophenylhydrazone, and with phenylcarbimide both forms yield the additive *compound*, COPh·CPh:CH·O·CO·NHPh, in the form of colourless plates, m. p. 129—130°.

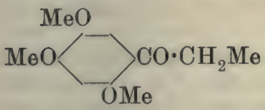
The *benzoyl* derivative, $C_{22}H_{16}O_3$, prepared from either the α- or β-compound, crystallises from benzene in colourless prisms, m. p. 105—106°, and the p-*nitrobenzoyl* derivative, $C_{22}H_{15}O_5N$, forms pale yellow needles, m. p. 118—119°. *Bromoformyldeoxybenzoin*,

COPh·CBrPh·CHO,

crystallises from light petroleum, and has m. p. 60—61°.

J. J. S.

Some Derivatives of Hydroxyquinol. GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 22—26. Compare this vol., i, 68).—The present paper deals with 2 : 4 : 5-trimethoxypropiophenone (annexed formula) and some of its derivatives.



The substance is obtained by the action of propionyl chloride on hydroxyquinol trimethyl ether in carbon disulphide solution in the presence of aluminium chloride. It crystallises in small, white needles, m. p. 106—108°, and is identical with the ketoasarone of Paolini (Abstr., 1910, i, 394). It gives a yellowish-green coloration with concentrated sulphuric acid, no coloration with ferric chloride, and with sodium nitroprusside and potassium hydroxide an intense red coloration which quickly becomes pale yellow. The *semicarbazone*, $C_{13}H_{19}O_4N_3$, forms colourless, hexagonal crystals, m. p. 166—167°. The semicarbazone obtained by the author from a sample of Paolini's ketoasarone also had this m. p., so that the semicarbazone of m. p. 182—183° described by the latter may be a stereoisomeride. *Trimethoxypropiophenoneoxime*, $C_{12}H_{17}O_4N$, forms colourless laminæ, m. p. 106—108°.

In the preparation of trimethoxypropiophenone a substance is also formed which crystallises in small, colourless needles, m. p. 110—112° (softening at 108—109°), and is probably 2 : 4 : 5-*trihydroxypropiophenone* 4 : 5-*dimethyl ether*. It dissolves in alkali with production of a yellow coloration, and yields a green coloration with ferric chloride.

R. V. S.

Relation between Chemical Constitution and Fastness to Light and Other Agencies of Polyhydroxybenzophenone Dyes. EDWIN R. WATSON and JATINDRA M. DUTTA (*J. Soc. Chem. Ind.*, 1911, 30, 196—197).—The following values have been obtained for the fastness of polyhydroxybenzophenones and xanthones to light. (*a*) Polyhydroxybenzophenones: 2 : 3 : 4-trihydroxy-III, 2 : 3 : 4 : 4′-tetrahydroxy-IV—V, 2 : 3 : 4 : 3′-tetrahydroxy-III—IV, 2 : 3 : 4 : 2′-tetrahydroxy-III, 2 : 4 : 3′ : 4′-tetrahydroxy-III, 2 : 3 : 4 : 2′ : 4′-pentahydroxy-II, 2 : 3 : 4 : 3′ : 4′ : 5′-hexahydroxy-I—II; (*b*) Polyhydroxyxanthones: 1 : 2-dihydroxy-II, 1 : 2 : 7-trihydroxy-II. The roman numerals indicate the fastness of each compound as recorded according to the British Association Committee's scale. It is evident that an increase in the number of hydroxyl groups tends to diminish the fastness to light, with the exception of the 2 : 3 : 4-trihydroxy-compound.

2 : 4 : 3′ : 4′-Tetrahydroxybenzophenone is the only dye appreciably faded by alkali, and those dyes which do not contain two hydroxyl groups in the ortho-position to one another and adjacent to the carbonyl group are most affected by acids. Most of the dyes are brightened and deepened by treatment with alkali, and the xanthones are not so fast to acid or light as the polyhydroxybenzophenones.

1 : 2 : 7-Trihydroxyxanthone is formed when the pentahydroxybenzophenone is heated with water in sealed tubes at 180—220° for

two and a-half hours. It crystallises from dilute alcohol in needles, is not molten at 285°, and its alkaline solutions are highly fluorescent.

J. J. S.

Ketens. XVI. Formation and Fission of Four-membered Rings. HERMANN STAUDINGER (*Ber.*, 1911, 44, 521—533).—The extreme ease with which the conversion of ethyl ethylketencarboxylate into ethyl 1 : 3-diethyl*cyclo*butan-2 : 4-dione-1 : 3-dicarboxylate and the reverse change occur (Abstr., 1910, i, 89) suggests that the two simple molecules may be united in the bimolecular substance by some kind of valency other than that operating between the ring carbon atoms of true *cyclo*butane derivatives. However, the decompositions described below show that the facile fission of ethyl diethyl*cyclo*butandionedicarboxylate is different in degree, not in kind, from the disruption of other *cyclo*butandiones obtained by the polymerisation of ketens, such as dimethylketen and diphenylketen. Attention is called to the polymerisation of phenylcarbimide, nitroso-compounds, and other substances, also to the additive compounds obtained from ketens and carbonyl compounds or anils, whereby β-lactones or β-lactams are produced (Abstr., 1909, i, 410; this vol., i, 215). In all of these cases four-membered heterocyclic substances are obtained which can be converted by comparatively simple means either into their generators or into a pair of new substances. A general connexion cannot be traced between the stability of the rings and their ease of formation; thus, for example, the β-lactams are easily obtained, and yet are very stable in comparison with the β-lactones, which are produced only with difficulty.

[With ST. BEREZA and MODRZEJEWSKI.]—Ethyl 1 : 3-diethyl*cyclo*butan-2 : 4-dione-1 : 3-dicarboxylate suffers rupture when shaken with water, yielding ethyl diethylacetonedicarboxylate and carbon dioxide. The molecule is also ruptured by the following reagents: boiling dilute barium hydroxide produces impure butyrone, cold alcoholic potassium hydroxide yields ethylmalonic acid (2 mols.), and alcoholic semicarbazide hydrochloride and potassium acetate cause the formation of *diethyl heptane-δ-one-γεε-tricarboxylatesemicarbazide*,

$$CO_2Et\cdot CHEt\cdot CO\cdot CEt(CO_2Et)\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2,$$

m. p. 140°, which develops a deep violet coloration with ferric chloride.

[With J. MAYER.]—2 : 2 : 4 : 4-Tetramethyl*cyclo*butan-1 : 3-dione (Abstr., 1906, i, 234) undergoes fission, aniline at 200° under pressure producing the anilide of *iso*butyric acid, and water at 160—180° or boiling dilute sodium hydroxide producing *iso*butyrone.

[With H. GÖLLER.]—2 : 2 : 4 : 4-*Tetraphenyl*cyclo*butan*-1 : 3-*dione*, $CPh_2<\begin{smallmatrix}CO\\CO\end{smallmatrix}>CPh_2$, m. p. 244—245°, is best obtained by heating diphenylketen-quinoline in benzene at 170° for eighty hours; amongst other substances, two polymerides are formed, one, m. p. 176° (as yet unexamined), in large amount, and the other, tetraphenyl*cyclo*butandione, in poor yield. It is very stable, but suffers depolymerisation when strongly heated. It is ruptured by 50% potassium hydroxide

and methyl alcohol on the water-bath, yielding *tetraphenylacetone*, $CO(CHPh_2)_2$, m. p. 135°, and a little diphenylacetic acid.

The additive compound of diphenylketen and *cyclo*pentadiene is converted, with considerable loss, into its generators by distillation at 160—180°/15 mm. in carbon dioxide.

The β-lactam of β-anilino-ααβ-triphenylpropionic acid is very stable, and can be distilled without appreciable decomposition. When, however, it is heated under a reflux condenser in a current of carbon dioxide, phenylcarbimide is removed, leaving triphenylethylene in the residue. The β-lactam of β-anilino-ααββ-tetraphenylpropionic acid (*loc. cit.*), by slow distillation in carbon dioxide, decomposes partly into tetraphenylethylene and phenylcarbimide, and partly into its generators, diphenylketen and benzophenoneanil. The β-lactam of β-*p*-dimethylaminoanilino-ααββ-tetraphenylpropionic acid (*loc. cit.*), however, decomposes at its m. p., or, better still, by distillation at 200—250°/15 mm., yielding diphenylketen; tetraphenylethylene is not formed, and *p*-dimethylaminophenylcarbimide cannot be detected with certainty. C. S.

Ketens. XVII. Phenylketen and Methylketen. HERMANN STAUDINGER (*Ber.*, 1911, 44, 533—543).—[With ST. BEREZA.]—Since ethyl ethylketencarboxylate is obtained so easily by heating its polymeride, ethyl 1 : 3-diethyl*cyclo*butan-2 : 4-dione-1 : 3-dicarboxylate (Abstr., 1910, i, 89), attempts have been made to prepare the very unstable phenylketen (Abstr., 1905, i, 444) in a similar manner. When an ethereal solution of phenylchloroacetyl chloride (which can be obtained in 66% yield by heating mandelic acid and phosphorus pentachloride [2 mols.] at 120—140° for about four hours, whereby the phosphoryl chloride is mainly removed as it is formed) is treated with zinc and kept for two hours after the addition of petroleum, the initially formed phenylketen polymerises completely. In addition to other substances, two polymerides are obtained, 1 : 3-*diphenyl*cyclo*butan*-2 : 4-*dione*, $CHPh<\substack{CO\\CO}>CHPh$, m. p. 73°, and its enolic modification, 1 : 3-*diphenyl*-Δ^1-cyclo*buten*-2-*ol*-4-*one*,

$$CHPh<\substack{C(OH)\\—CO—}>CPh.$$

The former does not react with ferric chloride, phenylcarbimide, or a solution of bromine, and yields a *disemicarbazone* (?), m. p. 220—230° (decomp.). It distils undecomposed at about 133° in a high vacuum, and does not yield phenylketen when more strongly heated. In other respects, however, it suffers fission like other polymeric ketens (compare preceding abstract); thus, with sodium hydroxide it yields dibenzyl ketone, and with methyl-alcoholic ammonia, diphenylacetoacetamide.

*Diphenyl*cyclo*butenolone*, which is also obtained by treating diphenyl*cyclo*butandione with 5% sodium hydroxide, separates from a mixture of benzene and ethyl acetate in crystals, m. p. 160°, containing 1 mol. of benzene. It develops a deep violet coloration with ferric chloride, decolorises a solution of bromine and of potassium permanganate, and is rapidly decomposed by warm water or dilute acids; its solution in

sodium hydroxide, however, can be boiled for some time without decomposition.

[With H. W. KLEVER and J. MAYER.]—Attempts to prepare methylketen give results similar to the preceding. A 0·4—0·5% ethereal solution can be obtained in 6—8% yield by treating α-bromopropionyl bromide in ethereal solution with zinc, and removing the methylketen and the solvent by distillation. From this solution, by fractional distillation in a high vacuum, fairly pure methylketen is obtained as a white, crystalline mass in a receiver cooled by liquid air; at higher temperatures the substance polymerises rapidly, yielding a small amount of a volatile substance with an unpleasant odour (*dimethyl*cyclo*butandione*?), together with 1 : 3-dimethyl-Δ^1-*cyclo*buten-2-ol-4-one (m. p. 140°, decomp. when pure). The latter polymeride is obtained better by keeping a dilute ethereal solution of methylketen for two days; it does not yield methylketen when heated, gives a deep-reddish violet coloration with alcoholic ferric chloride, and dissolves unchanged in warm sodium hydroxide.

C. S.

Ketens. XVIII. Decomposition of Benzilic Acid. HERMANN STAUDINGER (*Ber.*, 1911, 44, 543—547).—Nef has shown that the decomposition of benzilic acid by heating yields benzophenone, diphenylacetic acid, and a red resin, and explains the formation of these substances by assuming the initial production of diphenylmethylene, CPh_2⁚. This explanation is incorrect.

[With M. R. SCHÖLLER.]—When benzilic acid is heated at 155—165°/15 mm., it is partly converted into benzilide; this at a higher temperature decomposes into carbon dioxide and a ketone (unisolated), $CPh_2{<}^{CO}_{-O-}{>}CPh_2$, which suffers the typical fission of *cyclo*butanones (compare preceding abstracts), yielding diphenylketen and benzophenone, together with a red resin. In the decomposition of benzilic acid by heat, therefore, the diphenylacetic acid is produced by the interaction of the diphenylketen and the water formed during the decomposition.

[With H. GÖLLER.]—Benzilide is decomposed by water and benzene at 200°, yielding diphenylacetic acid, benzophenone, and other products. Benzilide must be boiled with 50% potassium hydroxide in order to reconvert it into benzilic acid. When benzilide is heated at 200° for two days with aniline (2 mols.) and benzene, it yields benzophenone and the anilide of diphenylacetic acid. When boiled with aniline under a reflux condenser for sixty hours, benzilide yields the anilide of anilinodiphenylacetic acid and a *substance*, m. p. about 200°.

C. S.

Isomerism of Naphthaquinone Derivatives. I. OSWALD MILLER (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 1418—1446).—The author has studied the transformations undergone by amino-α-naphthaquinoneimide (di-iminonaphthol) and its hydrochloride in aqueous solutions. This base acts as a mixture of isomerides, the action of water resulting in the simultaneous formation of 2-amino-α-naphthaquinone and 4-amino-β-naphthaquinone, in addition to ammonia.

According to Martius and Griess (*Annalen*, 1865, **134**, 377), and Graebe, and Ludwig (*Annalen*, 1870, **154**, 312), amino-α-naphthaquinoneimide hydrochloride forms anhydrous crystals, but the author finds that it crystallises from water or 95% alcohol as the dihydrate; it also forms crystals with $\frac{1}{2}H_2O$. In order to effect the separation of the base, the action of water on the hydrochloride was carried out in presence of excess of ammonia.

The results show that the yield of 2-amino-α-naphthaquinone (or 4-amino-β-naphthaquinone) increases in arithmetical progression as the concentration of the amino-α-naphthaquinoneimide hydrochloride diminishes (or increases) in geometrical progression. T. H. P.

Chrysophanic Acid. OTTO FISCHER, FERDINAND FALCO, and HANS GROSS (*J. pr. Chem.*, 1911, [ii], **83**, 208—214).—Chrysarobin and the chrysophanic acid derived from it have frequently been regarded as derivatives of α-methylanthracene. By demethylating chrysarobin by hydriodic acid under pressure and distilling the chrysophanhydranthrone obtained, after purification, with zinc dust, the authors have obtained β-methylanthracene, which is identified by its m. p., 203—204°, and by its conversion into β-methylanthraquinone and dibromomethylanthraquinone (Abstr., 1909, i, 563).

The oxidation of crude chrysophanhydranthrone by acetic and chromic acids on the water-bath yields chrysophanic acid containing as much as 10% of frangula-emodin; when the chrysophanhydranthrone has been purified, however, the amount of frangula-emodin in its products of oxidation is only 2—3% (compare Oesterle and Johann, Abstr., 1910, i, 860).

A solution of diacetylchrysophanic acid in acetic acid and acetic anhydride is oxidised by chromic acid to the diacetyl derivative (m. p. 246° [decomp.]) of rhein.

It only remains now to discover some means of smoothly eliminating carbon dioxide from rhein (which is most probably 1 : 8-dihydroxyanthraquinone-3-carboxylic acid) in order to settle definitely the constitutions of chrysophanic acid, aloe-emodin, and barbaloin. C. S.

Preparation of a Nitrogenous Oxidation Product of Acenaphthene. KALLE & CO. (D.R.-P. 228698. Compare Abstr., 1903, i, 500).—The oxidation of acenaphthene with potassium dichromate and acetic acid gives an unsatisfactory yield of acenaphthenequinone, which is not improved by substituting manganese dioxide and sulphuric acid or nitric acid as the oxidising agent. It is now found that by the action of nitrous acid esters in the presence of condensing agents (such as concentrated mineral acids, zinc chloride, or sodium ethoxide) on acenaphthene a yellow compound, m. p. about 220° and having the composition of acenaphthenequinoneoxime, is obtained; this on hydrolysis yields acenaphthenequinone. F. M. G. M.

o-Menthene-5-one. ARTHUR KÖTZ and ERWIN ANGER (*Ber.*, 1911, **44**, 466—467).—A number of new derivatives of the menthenone (1-methyl-2-*iso*propyl*cyclo*-Δ^6-hexene-5-one; compare Rabe and Rahm, Abstr., 1904, i, 747; 1905, i, 348; Merling, Abstr., 1905, i, 349;

Wallach, 1908, i, 813) obtained by Callenbach from Hagemann's ester have been prepared.

The *semicarbazone* occurs in two forms, melting at 138° and 152° respectively. The oxime has m. p. 90—91°, and the *hydrochloride* of this, m. p. 135—136°.

The corresponding *methyl*iso*propyl*cyclo*hexanone*, b. p. 95°/25 mm. or 204°/760 mm., furnishes an *oxime*, m. p. 75°, and a *benzylidene* derivative, m. p. 162°. T. A. H.

Terpenes and Ethereal Oils. CIII. Studies in the Fenchone Series. OTTO WALLACH (*Annalen*, 1911, **379**, 182—215).—The hydrocarbon C_9H_{16}, previously described (Abstr., 1909, i, 812; compare Bouveault and Levallois, *ibid.*, 1910, i, 572, 627, 686, 863), is now shown to be an equlibrium mixture. The proof is based on an examination of the products of oxidation with dilute permanganate at 0°, and on an examination of the nitroso-chlorides and their derivatives.

When oxidised with 2% permanganate solution at 0°, using 3 gram-atoms of oxygen for each gram-molecule of hydrocarbon, the chief products are unaltered hydrocarbon, a small amount of a glycol, and a mixture of two ketonic acids. One of the acids yields a *semicarbazone*, which crystallises from methyl alcohol in sparingly soluble needles, m. p. 173—175°, and an *oxime*, $C_9H_{17}O_3N$, in the form of plates, m. p. 118—119°. The acid has m. p. 19° and $[\alpha]_D^{18}$ +0·61°, and when oxidised with hypobromite yields Bouveault and Levallois' β-*iso*propylglutaric acid. The ketonic acid is therefore regarded as β-*iso*propyl-γ-acetylbutyric acid, $CH_3\cdot CO\cdot CH_2\cdot CHPr^{\beta}\cdot CH_2\cdot CO_2H$, although not identical with the acid described by Crossley (Trans., 1902, **81**, 676), and the hydrocarbon from which it is formed as 1-*methyl*-3-iso*propyl*-Δ^5-*cyclopentene*, $\begin{matrix} CH_2\cdot CH \\ | \\ C_3H_7\cdot CH\cdot CH_2 \end{matrix}\!\!>\!CMe$. The second ketonic acid yields a semicarbazone, which is amorphous, and has m. p. 138—140° or 150—152°, according to the method of heating. The corresponding oxime is an oil, and the acid itself has b. p. 175—180°/19 mm. and $[\alpha]_D$ −6·18°. On oxidation with hypobromite the ketonic acid yields a dibasic acid, which, after purification by conversion into its anhydride, has m. p. 92—93°; the anhydride crystallises from light petroleum, has m. p. 64—66°, and $[\alpha]_D^{17}$ +3·6°. The dibasic acid is regarded as *l*-α-*iso*propylglutaric acid (compare Abstr., 1903, i, 568), although the corresponding anilic acid has a lower m. p. than that previously given.

[With FRIEDRICH RITTER.]—The nitroso-chloride prepared by the action of concentrated hydrochloric acid at 0° to −10° on a mixture of the hydrocarbon, C_9H_{16}, glacial acetic acid, methyl alcohol, and freshly-prepared ethyl nitrite is not homogeneous; it consists of 40% of solid together with oily compounds. The solid appears to consist of a mixture of two nitroso-chlorides, but it has not been found possible to isolate both of these, as one is excessively unstable in solution. The nitroso-chloride, m. p. 115° (compare Abstr., 1909, i, 812), has $[\alpha]_D^{15}$ −272°, and yields a nitrolpiperidide, m. p. 160—161°. By decomposing the oxime (*loc. cit.*) with dilute sulphuric acid and

distilling in steam, a considerable amount of resin is formed, and comparatively small amounts of volatile products. These contain in addition to the ketone, $C_9H_{14}O$, a saturated nitrogen derivative,

$$C_9H_{15}ON,$$

b. p. 250—252°, which yields a *semicarbazone*, $C_{10}H_{18}ON_4$, in the form of colourless plates, m. p. 171—172°. The ketone reacts but slowly with an aqueous semicarbazide solution, but in methyl-alcoholic solution yields a *semicarbazone*, $C_9H_{14}\colon N\cdot NH\cdot CO\cdot NH_2$, in the form of colourless needles, m. p. 210—212°. The ketone regenerated from this semicarbazone has b. p. 191—192°, and an odour of thujone. If the nitroso-chloride is not purified by repeated crystallisation, the ketone prepared from it yields a mixture of two semicarbazones, namely, the one with m. p. 210—212°, and the one with m. p. 149—150° (Abstr., 1909, i, 813).

When reduced with zinc dust and glacial acetic acid, the crystalline nitroso-chloride yields an appreciable amount of a saturated ketone, together with a saturated primary amine and unsaturated ketone. The formation of the saturated ketone is represented by the following scheme: $>CCl\cdot\underset{|}{C}\colon N\cdot OH \longrightarrow >CH\cdot\underset{|}{C}\colon NH \longrightarrow >CH\cdot\underset{|}{C}\colon O$.

The saturated *ketone*, $C_9H_{16}O$, freed from the unsaturated compound by oxidation with 1% cold permanganate solution, has b. p. 184°, D^{20} 0·887, and n_D^{20} 1·4402. The ketone is, however, non-homogeneous, as it yields two semicarbazones. The one has m. p. 197—198°, and when hydrolised yields a ketone identical in all respects with dihydropulegenone (dihydrocamphorphorone) (Abstr., 1903, i, 568, 569). The formation of this ketone leads to the conclusion that the original hydrocarbon contains 1-methyl-3-*iso*propyl-Δ^1-*cyclo*pentene.

[With LUDWIG OLDENBERG.]—The *nitrile* of fencholic acid,

$$\begin{matrix} CHMe_2\cdot CH-CH_2 \\ \quad\quad | \\ \quad\quad CH_2\cdot CH_2 \end{matrix}\!\!>CMe\cdot CN,$$

prepared by the action of phosphoric oxide on the amide, is a colourless oil, b. p. 217—218°, has D^{19} 0·8660, n_D^{19} 1·4433, and $\alpha_D + 5°45'$ in a 1 dcm. tube. When reduced with sodium and alcohol, it yields 1-*methyl*-3-iso*propyl*cyclo*pentylmethylamine*, $C_{10}H_{19}\cdot NH_2$, with b. p. 204°, D^{20} 0·8500, and n_D^{20} 1·4545. The *hydrochloride* has m. p. 172—173°, the *benzoyl* derivative, m. p. 81—82°, and the *phenylcarbamide*, $NHPh\cdot CO\cdot NH\cdot C_{10}H_{19}$, m. p. 104—105°. The base readily absorbs carbon dioxide and combines with fenchylcarbimide, yielding the mixed *carbamide*, $C_9H_{17}\cdot NH\cdot CO\cdot NH\cdot C_{10}H_{19}$, m. p. 127—128°. The amine reacts with nitrous acid, yielding a mixture of an alcohol and a hydrocarbon. The alcohol, $C_{10}H_{20}O$, is tertiary, has b. p. 212—214°, D^{18} 0·903, and n_D^{18} 1·4603, and is probably either *p*-menthanol or a mixture of the meta- and para-compounds. The hydrocarbon, $C_{10}H_{18}$, has b. p. 175—176°, D^{20} 0·824, n_D^{20} 1·4571, and α_D + 32°13′ in a 1-dcm. tube, and is somewhat similar to carvomenthene. It is highly probable that by the action of nitrous acid on the base, the 5-membered has been transformed into a 6-membered ring (compare Abstr., 1907, i, 602). Fenchylamine (1-amino-1-methyl-3-*iso*propyl*cyclo*pentane) (*loc. cit.*, 812) reacts with nitrous acid, yielding the corresponding tertiary alcohol and hydrocarbon. 1-*Methyl*-3-iso*propyl*cyclo*pentan*-1-*ol*, $C_9H_{18}O$, has b. p.

185—187°, m. p. 76°, and the corresponding hydrocarbon, C_9H_{16}, which is probably a mixture of Δ^1- and Δ^5-derivatives, has b. p. 142—143°.

[With H. WIENHAUS.]—Different specimens of fenchonitrile differ somewhat in properties, as they are mostly mixtures. The α-compound forms a crystalline *nitrosochloride*, $C_{10}H_{15}N,NOCl$; this crystallises from acetone, has m. p. 123—124°, and is strongly lævorotatory. It reacts with alkalis or organic bases, regenerating the nitrile, which has D^{18} 0·749 and $[\alpha]_D^{18}$ +43°19′.

The nitrile prepared from the amide of fencholic acid, and also specimens prepared from fenchoneoxime, yield *dihydroxydihydrofenchonitrile*, $CN\cdot C_9H_{15}(OH)_2$, when oxidised with 1% permanganate at 0°. The hydroxynitrile forms a viscid, brown oil, b. p. 168—220°/12—14 mm., and crystallises from ethyl acetate in colourless, tabular prisms, m. p. 86°. The nitrile is readily hydrolysed by sodium hydroxide solution to *dihydroxydihydrofencholenic acid*, $CO_2H\cdot C_9H_{15}(OH)_2$, which crystallises from ethyl acetate in short, slender prisms, m. p. 111°. When boiled with dilute sulphuric acid, the hydroxynitrile yields a *ketonitrile*, m. p. 62—63°, the *semicarbazone* of which has m. p. 204—206°. When further oxidised with permanganate, the hydroxynitrile yields a *ketonitrile-carboxylic acid*, $C_{10}H_{15}O_3N$, the *oxime* of which has m. p. 260—262°, and the *semicarbazone*, m. p. 190—192°.

β-Fencholenic acid, when reduced with hydrogen and colloidal palladium, yields fencholic acid, and is, therefore, presumably $\begin{array}{l}CMe_2{:}C—CH_2\\ \quad\;\; CH_2\cdot CH_2\end{array}\!\!>CMe\cdot CO_2H$. α-Fencholenic acid, when reduced in a similar manner, yields a product which appears to be identical with Mahla's dihydrofencholenic acid (Abstr., 1902, i, 107). The amide has m. p. 133—134°.

The amides of α- and β-fencholenic acids are reduced more readily than the acids themselves. J. J. S.

Terpenes and Ethereal Oils. CIV. OTTO WALLACH (*Annalen*, 1911, **379**, 215—228).—[With PAUL VIRCK.]—The author confirms Angeli and Rimini's statement (Abstr., 1897, i, 88; compare Rimini, 1900, i, 554; Tiemann and Mahla, *ibid.*, 1897, i, 85) that the isomeric nitro-imines, $C_{10}H_{16}O_2N_2$, from fonchoneoxime and camphoroxime yield the same unsaturated ketone, 1-methyl-5-*iso*propyl-Δ^6-*cyclo*hexen-2-one*iso*camphor, when treated with concentrated sulphuric acid and then poured into water. It is shown that the ketone is not formed by the acid, but by the subsequent treatment with water. The compound, $C_{10}H_{16}O_2N_2$, from fenchoneoxime crystallises from dilute methyl alcohol, has m. p. 59—60° (Rimini, 66—67°; Tiemann and Mahla, 58°), and $[\alpha]_D$ +25·83°. The ketone, although optically active, on oxidation yields *dl-α-iso*propylglutaric acid (compare Angeli and Rimini). The ketone is extremely unstable; it has D^{20} 0·9260, n_D^{20} 1·4758, and b. p. 216°. The b. p. is somewhat lower than that of the isomeride of the para-series, namely, carvotanacetone, b. p. 228°. The b. p. of 1-methyl-3-*iso*propyl-Δ^6-hexene-5-one, namely, 244—245° (Knoevenagel, Abstr., 1893, i, 419), is too high.

1-Methyl-5-*iso*propyl-Δ^6-*cyclo*hexene-2-one forms an oily, additive compound with hydrogen sulphide, and also yields a solid condensation

product with benzaldehyde. When reduced with sodium and moist ether, the ketone yields the saturated alcohol, 1-*methyl*-5-iso*propyl*cyclo*hexane-2-ol*, $CHMe_2 \cdot CH<\begin{matrix}CH_2 \cdot CHMe \\ CH_2 - CH_2\end{matrix}>CH \cdot OH$, and this on oxidation yields 1-*methyl*-5-iso*propyl*cyclo*hexan-2-one*, $C_{10}H_{18}O$, b. p. 211—212°, D^{21} 0·8885, n_D^{20} 1·4466. The *semicarbazone* has m. p. 162—163°. The alcohol has b. p. 215—216°, D^{21} 0·889, and n_D^{20} 1·4563 (compare Spica, Abstr., 1902, i, 43).

[With Friedrich Henjes.]—It is pointed out that various unsaturated nitriles of the camphor series combine readily with nitrosyl chloride. *Menthonitrile nitrosochloride*, $C_{10}H_{17}N,NOCl$, crystallises from methyl alcohol, and has m. p. 96—97°; the corresponding *nitrolpiperidide*, $C_{10}H_{17}N \cdot NO \cdot C_5NH_{10}$, has m. p. 83—85°. The nitrosochloride when treated with alkalis or reducing agent regenerates the nitrile. *Citronellalnitrile nitrosochloride*, $C_{10}H_{17}N \cdot NOCl$, has m. p. 106°; the *nitrolpiperidide*, m. p. 88—90°; and the *nitrol*-p-*toluidide*, m. p. 107—108°. Camphonitrile and pulegenonitrile yield bluish-green oils when treated with nitrosyl chloride. J. J. S.

Action of Piperidine on *d*-Pinene Chloro-oxime. L. V. Buschueff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1447—1448).—In Schimmel's Bericht (Oct., 1910, 171) it is stated that the results of the author's investigations on the action of piperidine on *d*-pinene chloro-oxime (Abstr., 1910, i, 122) confirm those of Wallach (Abstr., 1888, 1098). The author points out, however, that he obtained nitrosopinene and pinene nitrolpiperidine as the products of this reaction (compare Golubeff, Abstr., 1908, i, 902), whilst Wallach obtained pinene nitrolpiperidine only. T. H. P.

New Constituent of Angelica Root Oil. E. Böcker and Alfred Hahn (*J. pr. Chem.*, 1911, [ii], **83**, 243—248).—The least volatile fraction of angelica root oil deposits, after long keeping, a small amount of a crystalline substance, m. p. 84° (compare Ciamician and Silber, Abstr., 1896, i, 595), which exhibits the properties of an unsaturated γ-lactone. It has the formula $C_{15}H_{16}O_3$, is not changed by hot or cold aqueous alkalis or cold alcoholic potassium hydroxide, but is hydrolysed by boiling *N*/2-alcoholic potassium hydroxide (saponification number 238), the product regenerating the lactone by acidification. It forms a *dibromide*, $C_{15}H_{16}O_3Br_2$, m. p. 143—145°, and an additive *compound*, $C_{15}H_{17}O_3Cl$, m. p. 101°, with ethereal hydrogen chloride. C. S.

Constituents of Essential Oils. Identity of the Alcohol, $C_{10}H_{16}O$, of Gingergrass Oil with Perilla Alcohol. Tricyclene-carboxylic Acid. Friedrich W. Semmler and B. Zaar (*Ber.*, 1911, **44**, 460—463).—The supposed dihydrocuminol obtained by Schimmel & Co. from gingergrass oil (Abstr., 1905, i, 536) and examined by Wahlbaum and Hüthig (*loc. cit.*, p. 53) has been re-investigated, and proved to be identical with the alcohol obtained by reducing Perilla-aldehyde (Semmler and Zaar, this vol., i, 218). The alcohol, purified as far as possible from geraniol, has the following constants: b. p.

107—110°/12·5 mm., D^{20} 0·946, n_D 1·4968, a_D $-7°$ (100 mm.). The low optical activity is doubtless due to partial racemisation. With phosphorus pentachloride it gives a *chloride*, $C_{10}H_{15}Cl$, b. p. 97—102°/14 mm., D^{20} 0·9848, n_D 1·50058, a_D $-16°$ (100 mm.), and this, on reduction with sodium in alcohol, furnishes limonene, identified by means of its tetrabromide. These data, and the fact that the alcohol yields Perilla-aldehyde on oxidation, prove that it is identical with Perilla alcohol.

Comparison of tricyclenecarboxylic acid (Bredt and May, Abstr., 1910, i, 32) with teresantalic acid proves that the two are not identical (compare Semmler, *Äther. Öle*, 1906, ii, 90, and Abstr., 1907, i, 703, 1062). T. A. H.

Action of Chromyl Chloride on India-rubber. DAVID SPENCE and J. C. GALLETLY (*J. Amer. Chem. Soc.*, 1911, **33**, 190—194).—Although the action of chromyl chloride on terpenes has been extensively studied, its action on caoutchouc has not hitherto been investigated.

When chromyl chloride is added to a solution of caoutchouc in carbon disulphide, the *compound*, $C_{10}H_{16},2CrO_2Cl_2$, rapidly separates as a voluminous, dark brown precipitate, which is insoluble in organic solvents; on exposure to the air it absorbs moisture, and rapidly undergoes decomposition. The same product was obtained from several caoutchoucs of different botanical origin. When the compound is treated with water, it is immediately decomposed with formation of a dark green solution, from which, on heating, a brown, gummy mass separates. By extracting the latter product with ether or chloroform, a *substance* is obtained in an impure state which gives the reactions of an aldehyde, and when treated with phenylhydrazine yields a crystalline compound, m. p. about 92°. If the solution obtained by the action of water on the chromyl chloride compound is submitted to dialysis, an opalescent, colloidal solution is produced, from which an insoluble *substance* has been isolated containing definite proportions of chromium and chlorine. The investigation is being continued. E. G.

Vulcanisation of Caoutchouc. B. V. BYSOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1358—1362. Compare Abstr., 1910, i, 865).—The author finds that, given constant conditions of vulcanisation, the ratio between the proportions of total and free sulphur (extractable by acetone) is approximately constant. In preparations containing small amounts of sulphur, this ratio increases as the total proportion diminishes.

When caoutchouc is vulcanised with steam under three atmospheres pressure, the curve showing the relation of the proportion of free sulphur to the time is asymptotic to the time axis. Hence, in order to compare the proportions of free sulphur in different vulcanised caoutchoucs, it is necessary to vulcanise until the amount of free sulphur becomes practically constant; under the above conditions this requires two hours.

A series of mixtures of caoutchouc and sulphur containing 1·0, 1·2, 1·4, 1·6, 1·8, and 2% of sulphur respectively were vulcanised with steam as above. Examination of the various samples showed that

(total sulphur)^n/(free sulphur) = a constant. The value of n was 3·1, and that of the constant, 26·692, but these values may vary with the kind of caoutchouc and with the method of vulcanisation.

T. H. P.

Bixin. ALFR. HEIDUSCHKA and H. RIFFART (*Arch. Pharm.*, 1911, **249**, 43—48).—The results of an investigation of the action of halogens on bixin are given, and the old formula, $C_{28}H_{34}O_5$, is adopted for this dye in preference to $C_{29}H_{34}O_5$ suggested recently by van Hasselt (Abstr., 1909, i, 598).

On adding bromine to bixin, dissolved in chloroform, a colourless, amorphous compound, $C_{28}H_{34}O_5Br_{10},4HBr$, m. p. 143°, is obtained. This on heating at 100° decomposes, yielding a yellow *decabromide*, which can be crystallised from alcohol, but decomposes when heated or when kept (compare van Hasselt, *loc. cit.*). The analogous *substances*, $C_{28}H_{34}O_5Cl_{10},4HCl$, m. p. 91°, and $C_{27}H_{32}O_5Cl_{10},4HCl$, m. p. 102°, the latter obtained from *nor*bixin, are similarly prepared by the action of chlorine and are amorphous.

Bixin and *nor*bixin each combine with 11 mols. of hydrogen chloride to form amorphous, pale yellow *additive products*; the one has m. p. 74°, and the other, m. p. 108°.

T. A. H.

The Benzotetronic Acid Group. II. Ketonic Hydrolysis of Benzotetronic Acid [4-Hydroxycoumarin] and its Homologues. RICHARD ANSCHÜTZ and MAX EUGEN SCHOLL (*Annalen*, 1911, **379**, 333—350. Compare Abstr., 1909, i, 660).—*o*-Hydroxyacetophenone and its three methyl derivatives can be obtained by hydrolysing benzotetronic acid and its methyl derivatives with potassium hydroxide solution at relatively high temperatures. When the ethyl ether of benzotetronic acid [4-ethoxycoumarin] is hydrolysed, the first product is the free acid, and finally *o*-hydroxyacetophenone; the intermediate product, *o*-hydroxybenzoylacetic acid,

$$OH\cdot C_6H_4\cdot CO\cdot CH_2\cdot CO_2H,$$

cannot be isolated. For the preparation of the hydroxyacetophenones it is not necessary to prepare the benzotetronic acids, but to start with the condensation products of acetylated salicylic acid chlorides and ethyl sodiomalonate.

Methyl 4-hydroxycoumarin-3-carboxylate, $C_6H_4<\begin{matrix}O\text{——}CO\\ C(OH){:}C\cdot CO_2Me\end{matrix}$, prepared from acetylsalicyl chloride and methyl sodiomalonate crystallises from alcohol in colourless needles, m. p. 136°; when hydrolysed with 33% potassium hydroxide solution at 115° for ten hours, it yields potassium benzotetronate, but at 180° gives an 80% yield of *o*-hydroxyacetophenone, b. p. 96—97°/10 mm. (compare Friedländer and Neudörfer, Abstr., 1897, i, 424); the oxime has m. p. 117°, not 112° (Dunstan and Henry, Trans., 1899, **75**, 66), and the phenylhydrazone is only sparingly soluble in sodium hydroxide solution. The *benzoyl* derivative, $COPh\cdot O\cdot C_6H_4\cdot COMe$, crystallises from alcohol in colourless needles, m. p. 88°; the *semicarbazone*,

$$OH\cdot C_6H_4\cdot CMe{:}N\cdot NH\cdot CO\cdot NH_2,$$

also crystallises in colourless needles, and when heated at 225° is rapidly transformed into *o-hydroxyacetophenoneazine*,

$$N_2(:CMe\cdot C_6H_4\cdot OH)_2,$$

which is also formed when the hydroxyacetophenone is shaken for several days with an aqueous solution of hydrazine sulphate. The azine crystallises from alcohol in glistening, pale yellow needles, m. p. 197—198°.

Acetyl-*o*-cresotic [2-acetoxy-*m*-toluic] acid,

$$OAc\cdot C_6H_3Me\cdot CO_2H\ [CO_2H : OAc : Me = 3 : 2 : 1],$$

crystallises from benzene in colourless needles, m. p. 113°, and reacts with phosphorus pentachloride in the presence of light petroleum, yielding the *chloride*, $OAc\cdot C_6H_3Me\cdot COCl$, which can be distilled under extremely low pressures.

Methyl 4-*hydroxy*-8-*methylcoumarin*-3-*carboxylate*,

$$C_6H_3Me<\begin{matrix}O\text{———}CO\\ C(OH):\dot{C}\cdot CO_2Me\end{matrix},$$

crystallises from alcohol in colourless plates, m. p. 109°, and with aqueous potassium hydroxide solution at 100° yields 4-*hydroxy*-8-*methylcoumarin* (3-*methylbenzotetronic acid*), $C_{10}H_8O_3$, which crystallises from water in colourless, glistening needles, m. p. 228° (decomp.). 2-*Hydroxy*-3-*methylacetophenone*, $OH\cdot C_6H_3Me\cdot COMe$, has b. p. 106—107°/10·5 mm.; the *phenylhydrazone*, $C_{15}H_{16}ON_2$, crystallises from alcohol in yellow needles, m. p. 122°; the *semicarbazone*, $C_{10}H_{13}O_2N_3$, in colourless needles, m. p. 228°, and the *azine*,

$$C_{18}H_{20}O_2N_2,$$

in slender, orange-yellow needles, m. p. 237°.

Methyl 4-*hydroxy*-7-*methylcoumarin*-3-*carboxylate*, $C_{10}H_{12}O_2$, crystallises from alcohol in colourless needles, m. p. 208° (decomp.), and on hydrolysis with potassium hydroxide solution at 200° yields 2-hydroxy-4-methylacetophenone, which has b. p. 105—106°/9 mm. (compare Eykman, Abstr., 1904, i, 664). The *phenylhydrazone* of the latter crystallises from alcohol in yellow, glistening plates, m. p. 105°; the *semicarbazone* in colourless needles, m. p. 214°, and the *azine*, in slender, yellow needles, m. p. 219°.

Methyl 4-*hydroxy*-6-*methylcoumarin*-3-*carboxylate*, $C_{10}H_{12}O_2$, obtained from acetyl *p*-cresotyl chloride, crystallises from alcohol in soft, felted needles, m. p. 210° (decomp.), and on hydrolysis yields 2-hydroxy-5-methylacetophenone (compare Auwers and Müller, Abstr., 1909, i, 223). The *benzoyl* derivative of the latter, $C_{16}H_{14}O_3$, crystallises from alcohol in stout, colourless prisms, m. p. 65°. The *oxime*,

$$OH\cdot C_6H_3Me\cdot CMe:N\cdot OH,$$

forms small, colourless needles, m. p. 145°; the *semicarbazone*,

$$C_{10}H_{13}O_2N_3,$$

in colourless, rhombic crystals, m. p. 212°, and the *azine*, $C_{18}H_{20}O_2N_2$, in orange-yellow needles, m. p. 223°. J. J. S.

The Grignard Reaction. Syntheses of Fluoran. ENOS FERRARIO [and, in part, M. NEUMANN] *Gazzetta*, 1911, 41, i, 1—11).—By the series of reactions described below, the author has effected the synthesis of fluoran. Another method by which this was attempted yielded only phenolphthalein diphenyl ether.

Magnesium *o*-methoxyphenyl iodide (in ethereal solution) reacts with phthalic anhydride (in benzene solution), yielding 2 : 2′-*dimethoxyphthalophenone*, $C_{22}H_{18}O_4$, which crystallises in colourless needles or in small cubes, m. p. 145—146°, and dissolves in concentrated sulphuric acid, producing a bluish-violet coloration. On reducing it with zinc and glacial acetic acid, 2 : 2′-*dimethoxytriphenylmethane-2″-carboxylic acid*, $(OMe\cdot C_6H_4)_2CH\cdot C_6H_4\cdot CO_2H$, is obtained; it forms colourless needles, m. p. 249—250° (on rapid heating; if the m. p. is taken slowly, the substance begins to melt at 235°, is almost melted at 240°, and completely so at 245°). The acid forms *potassium* and *sodium* salts, which crystallise in laminæ; amorphous *barium* and *calcium* salts, and a *silver* salt, which blackens quickly. The *methyl* ester has m. p. 149—150°. When the acid is demethylated, preferably by heating it with hydrochloric acid (D 1·4) for two hours in a sealed tube at 130—140°, it yields fluoran. This synthetic fluoran crystallises with two molecules of alcohol, part of which it retains for a time even when fused.

Phenolphthalein diphenyl ether is obtained by heating together phthalic anhydride, phenyl ether, and zinc chloride for six hours at 180—190°, and also (but not so well) by the action of phthalyl chloride on phenyl ether. It has m. p. 105—106°, and dissolves in concentrated sulphuric acid, producing a cherry-red coloration.

R. V. S.

Thalleioquinine. Ezio Comanducci (Pamphlet, 1910, 7 pp. Compare Abstr., 1910, i, 581).—The author gives a more detailed account of the properties of this substance, and of its behaviour with a number of reagents. It has m. p. 148—149° (corr., sintering at 130°). Analysis gave C 59·00%, H 8·47%, N 7·53—8·52%, Cl 3·88—4·13%. In alcoholic solution the compound has $[\alpha]_D^{21}$ − 187·5°. The molecular weight determined ebullioscopically in various solvents varies from 300—450. The *hydrochloride* is an amorphous residue, m. p. 120—122° (sintering at 100°), and has $[\alpha]_D^{21}$ − 255·1°. The *platinichloride* is a greenish-white precipitate, which becomes brown at 230°, sinters at 240°, and melts at 263°. The *picrate* is an amorphous, yellowish-green powder, m. p. 135° (sintering at 130°). An account is given of the absorption spectrum of the substance and also of that of quinine.

R. V. S.

Volatility of Cocaine. H. C. Fuller (*J. Ind. Engin. Chem.*, 1910, 2, 426).—Attention is drawn to the fact that cocaine is appreciably volatile at temperatures of, and exceeding, 98°, a fact which is of importance in the method usually employed in the assay of coca leaves. Experiments showed that cocaine can be heated at 60°, 80°, and 90° without loss of weight, and the conclusion is drawn that these residues should be dried at a temperature not exceeding 90°, or, preferably, desiccated, without heating, over sulphuric acid.

F. M. G. M.

Alkaloids of the Perennial Papaveraceæ. Papaver orientale and P. lateritium. Johannes Gadamer (*Arch. Pharm.*, 1911, 249, 39—42).—With a view to obtaining data bearing on the function and method of formation of alkaloids in plants, the author

proposes to examine a number of the perennial plants of the Papaveraceæ. The distribution of protopine will be specially studied. This alkaloid does not occur in *P. orientale* or *P. lateritium*.

[With WALTER KLEE.]—*P. orientale* contains an *alkaloid*, m. p. 204—205°, which separates from ether in colourless crystals, and, since it is soluble in alkali, must contain a phenolic hydroxyl group. *P. lateritium* also contains a phenolic base, or mixture of bases, from which no crystalline substance could be separated. T. A. H.

Corydalis Alkaloids. Corycavidine, a New Alkaloid of the Corycavine Series. JOHANNES GADAMER (*Arch. Pharm.*, 1911, **249**, 30—39).—The mixed amorphous alkaloids of *Corydalis cava* tubers, prepared as described already (Abstr., 1902, i, 306), on conversion into thiocyanates can be separated into two groups, one giving crystalline thiocyanates, soluble with difficulty in alcohol, and the other readily soluble, amorphous thiocyanates. From the second group a new alkaloid, corycavidine, closely related to corycavamine, has been isolated and characterised.

Corycavidine, $C_{22}H_{25}O_5N$, $[\alpha]_D^{20}$ $+203{\cdot}1°$ in chloroform, crystallises from hot chloroform with $1CHCl_3$ on addition of alcohol. When heated it changes at 209°, and melts at 212—213°. The change at 209° is into *i*-corycavidine (m. p. 193—195°, after re-crystallisation), and resembles that brought about by heating corycavamine (Abstr., 1902, i, 391). The *hydrochloride*, *nitrate*, and *sulphate* were prepared; the two former are crystalline. The *aurichloride*, $BHAuCl_4$, is a red powder, which sinters at 85° and decomposes at 170°.

Corycavidine contains two methoxyl groups, and a methyl group attached to the *N*-atom. It appears to be corycavamine, in which a dioxymethylene group is replaced by two methoxyl groups, and this view finds support in the similarity of the colour reactions of the two alkaloids and their similar behaviour on heating.

Corycavidine, like corycavamine, is unaffected by hot iodine solution. With methyl iodide it gives a *methiodide*, $B{\cdot}CH_3I,3H_2O$, m. p. 207—210° (decomp.), which is optically inactive, and forms small, colourless crystals from alcohol. When boiled with alkali hydroxide, the methiodide gives the corresponding *methine base*, m. p. 141·5—142·5°, which forms colourless crystals from ether, and with methyl iodide furnishes a methiodide, which was not isolated, but treated directly with alkali, when it decomposed, giving trimethylamine and a neutral substance. The latter polymerised very readily, forming a yellow, amorphous mass, and on oxidation with permanganate yielded a crystalline acid and a crystalline neutral substance, probably a glycol.

T. A. H.

Constitution of Tropilen. ARTHUR KÖTZ and RICHARD ROSENBUSCH (*Ber.*, 1911, **44**, 464—466).—Tropilen, $C_7H_{10}O$, the final product of the "exhaustive methylation" of tropine, was supposed by Merling to be tetrahydrobenzaldehyde (Abstr., 1892, i, 358), and by Willstätter (Abstr., 1898, i, 540) to be *cyclo*heptenone,

$$\left.\begin{array}{l}CH_2{\cdot}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH{=}CH\end{array}\right>CO.$$

Willstätter's attempt to confirm this formula by the reduction of tropilen to suberone (Abstr., 1901, i, 649) was unsuccessful. By the use of Paal's reduction method with palladium as catalyst the authors have now effected this reduction and confirmed Willstätter's formula.

T. A. H.

Preparation of *iso*Sparteine. Action of Methyl Iodide on the Base. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1911, **152**, 386—387).—A 90% yield of *iso*sparteine can be obtained from α-methylsparteine by heating the dihydrochloride of the latter at 220—230° in a current of hydrogen chloride.

When *iso*sparteine is boiled with methyl iodide in methyl-alcoholic solution, a mixture of two methiodides is formed; the α-compound has $[\alpha]_D$ − 16·8°, and is identical with the methiodide previously described (Abstr., 1908, i, 44), whilst the isometic iso*sparteine α′-methiodide* has $[\alpha]_D$ −33·3°. The two substances are separated by taking advantage of the different solubilities of their hydriodides in water.

W. O. W.

***iso*Sparteine. A Case of Stereoisomerism of Nitrogen.** CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1911, **152**, 527—529. Compare preceding abstract).—The two isomeric α- and α′-methiodides of *iso*sparteine are now shown to owe their existence to a different spatial arrangement with regard to one nitrogen atom. If they correspond with the fixation of methyl iodide on two different nitrogen atoms, the bases arising by decomposition of the corresponding methyl*iso*sparteinium hydroxides should not be identical. It has been found, however, that α-methylsparteine is produced when either the α- or α′-hydroxide is heated in a vacuum. In the latter case a new base, *methyl*iso*sparteine*, $C_{16}H_{28}N_2$, is also formed. This has m. p. 24°, $[\alpha]_D$ + 23·6°, and may be separated from α-methylsparteine by mixing with methyl iodide in methyl-alcoholic solution, when *methyl*iso*sparteine dimethiodide*, $C_{16}H_{28}N_2,2MeI$, m. p. 281—282° (decomp.), is formed. A better method, which allows of isolating both bases, consists in heating with dilute sulphuric acid, when α-methylsparteine alone is converted into the methosulphate.

*Methyl*iso*sparteine dipicrate* has m. p. 203°. The *platinichloride* blackens at 240°, and has m. p. 256° (decomp.). W. O. W.

Synthesis of Pyrrole and Furfuran Derivatives from Dichloroethyl Ether, Ethyl Acetoacetate, and Ammonia. ERICH BENARY (*Ber.*, 1911, **44**, 493—496).—By the interaction of dichloroethyl ether, ethyl acetoacetate, and aqueous ammonia in the cold, a mixture of ethyl 2-methylpyrrole-3-carboxylate and ethyl 2-methylfurfuran-3-carboxylate is obtained. The mechanism of the reaction is precisely similar to that between chloroacetone, ethyl acetoacetate, and ammonia studied by Hantzsch (Abstr., 1890, i, 1165) and Feist (Abstr., 1902, i, 488).

Ethyl 2-methylpyrrole-3-carboxylate crystallises in colourless leaflets, m. p. 78—79°, and dissolves in concentrated sulphuric acid with a

reddish-violet coloration. It is hydrolysed to the corresponding acid already described by Ciamician (*Ber.*, 1878, **14**, 1056).

Ethyl 2-methylfurfuran-3-carboxylate is an oil, b. p. 85—87°/20 mm. The corresponding acid forms colourless needles, m. p. 101—102° (Plancher and Albini, Abstr., 1904, i, 334). E. F. A.

Synthesis of Pyridine Derivatives from Dichloroethyl Ether and Ethyl-β-aminocrotonate. ERICH BENARY (*Ber.*, 1911, **44**, 489—493).—By the interaction of ethyl-β-aminocrotonate and 1 : 2-dichloroethyl ether, *ethyl* 2 : 6-*dimethyl*-4-*chloromethyldihydropyridine*-3 : 5-*dicarboxylate*, $NH<\begin{matrix}CMe{:}C(CO_2Et)\\CMe{:}C(CO_2Et)\end{matrix}>CH\cdot CH_2Cl$, is obtained in tiny, colourless needles, m. p. 133—134°. On oxidation with dilute nitric acid (D 1·17), the corresponding *ethyl* 2 : 6-*dimethyl*-4-*chloromethylpyridine*-3 : 5-*dicarboxylate* is formed; it is a colourless, viscid oil, m. p. 197—198°. It was mixed with a small quantity of a chlorine-free substance crystallising in needles, m. p. 72—73°. A further by-product of the oxidation is *ethyl* 2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*-4-*methylnitrolic acid*,

$$N\leqslant\begin{matrix}CMe\cdot C(CO_2Et)\\CMe{:}C(CO_2Et)\end{matrix}\geqslant C\cdot C(NO_2){:}N\cdot OH,$$

which crystallises in colourless needles, m. p. 110° (decomp.); it gives a red coloration with alkali hydroxide only in concentrated solution. When boiled with dilute nitric acid the *diethyl* ester of 2 : 6-*dimethylpyridine*-3 : 4 : 5-*tricarboxylic acid* is formed,

$$N\leqslant\begin{matrix}CMe\cdot C(CO_2Et)\\CMe{:}C(CO_2Et)\end{matrix}\geqslant C\cdot CO_2H;$$

it crystallises in tiny needles, m. p. 181° (decomp.).

Ethyl 2 : 6-*dimethyl*-4-*iodomethylpyridine*-3 : 5-*dicarboxylate* is obtained by the interaction of the corresponding chloro-compound with sodium iodide in acetone solution; it crystallises in granular crusts, m. p. 77—78°.

Ethyl 1 : 2 : 6-*trimethyl*-4-*chloromethyldihydropyridine*-3 : 5-*dicarboxylate*, $NMe<\begin{matrix}CMe{:}C(CO_2Et)\\CMe{:}C(CO_2Et)\end{matrix}>CH\cdot CH_2Cl$, from dichloroethyl ether and ethyl β-methylaminocrotonate, crystallises in four-sided platelets, m. p. 88—89°. E. F. A.

Condensation of Crotonaldehyde with Ammonia and Ethyl Acetoacetate. E. GRISHKEWITSCH-TROCHIMOWSKY (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1377—1380).—*Ethyl* 2 : 6-*dimethyl*-4-*allyldihydropyridine*-3 : 5-*dicarboxylate*,

$$CHMe{:}CH\cdot CH<\begin{matrix}C(CO_2Et){:}CMe\\C(CO_2Et){:}CMe\end{matrix}>NH,$$

prepared by the condensation of crotonaldehyde with ammonia and ethyl acetoacetate, forms colourless crystals, m. p. 144·5—145·5°. When oxidised it yields a viscous, pale yellow liquid, b. p. about 205°/45 mm., and, when treated with platinum chloride in concentrated hydrochloric acid solution, it gives *ethyl* 2 : 6-*dimethyl*-4-*allylpyridine*-3 : 5-*dicarboxylate platinichloride*, $C_{16}H_{21}O_4N,H_2PtCl_6$, forming orange needles, m. p. 177·5—178°.

When the dihydropyridinedicarboxylic ester is hydrolysed and the salt subsequently subjected to dry distillation with slaked lime, it yields a colourless liquid, b. p. 175—178°, which is probably 2:4:6-*trimethylpyridine*; it forms a *platinichloride*, m. p. about 220° (decomp.), an *aurichloride*, and a *mercurichloride* compound, m. p. 155—155·5°.

T. H. P.

New Diethyltrimethylenepyrrole Derivatives. MARIO GHIGLIENO (*Atti R. Accad. Sci. Torino*, 1911, 46, 87—95).—In order to test the accuracy of the explanation given (Abstr., 1910, i, 427) for the existence of two isomeric forms of 3:5-dicyano-4-methyl-4-ethyltrimethylenedicarbonimide and of similar methylethyl compounds, the author has examined various diethyl derivatives homologous with methylethyl derivatives already described (*loc. cit.*; Abstr., 1910, i, 505). The results confirm the hypothesis of spatial isomerism, since in no case could two isomeric diethyl derivatives be prepared.

The *mono-amide* of 3:5-*dicarboxy*-4:4-*diethyltrimethylenedicarbonimide*, $NH<\begin{matrix}CO\cdot C(CO\cdot NH_2)\\ | \\ CO\cdot C(CO_2H)\end{matrix}>CEt_2$, prepared by the action of dilute sodium hydroxide solution on the corresponding 3:5-dicyano-compound, has m. p. 247—250° (Maquenne block), and behaves as a dibasic acid, owing to the mobility of the iminic hydrogen under the influence of the neighbouring groups; the second basicity is, however, weak, and, in $N/10$-solution, can only be estimated to the extent of about 50% by means of sodium hydroxide and phenolphthalein. The *silver*, $C_{11}H_{12}O_5N_2Ag_2,H_2O$, lead, copper, and barium salts are all sparingly soluble.

4:4-*Diethyltrimethylenedicarbonimide*-3:5-*dicarboxylic acid*,

$$NH<\begin{matrix}CO\cdot C(CO_2H)\\ | \\ CO\cdot C(CO_2H)\end{matrix}>CEt_2,$$

obtained by the action of nitrous acid on the preceding compound, forms colourless needles $(+1\frac{1}{2}H_2O)$, the anhydrous acid having m. p. 188—189° (Maquenne block); it behaves as a dibasic acid, although not so sharply as the corresponding methylethyl homologue, and forms insoluble lead, copper, silver, and mercurous salts. When heated it loses $2CO_2$, forming 4:4-*diethyltrimethylenedicarbonimide*,

$$NH<\begin{matrix}CO\cdot CH\\ | \\ CO\cdot CH\end{matrix}>CEt_2,$$

as a yellow, semi-fluid mass; this compound gives sparingly soluble *silver*, $C_9H_{12}O_2NAg$, lead, copper, and zinc salts.

T. H. P.

Constitution of the Pseudo-ammonium Bases. ADOLF KAUFMANN and PAUL STRÜBIN (*Ber.*, 1911, 44, 680—690).—The constitution of the pseudo-ammonium bases has long been a subject of discussion (compare Hantzsch and Kalb, Abstr., 1900, i, 113). In particular, the first product formed on oxidation of the alkylquinolinium bases has been assumed to be a carbinol base, $C_6H_4<\begin{matrix}CH:CH\\ | \\ NR\cdot CH\cdot OH\end{matrix}$ (Decker, Hantzsch), or an aldehyde base with the

pyridine ring opened, $NHR\cdot C_6H_4\cdot CH{:}CH\cdot CHO$ (Roser, Gadamer, Reissert), or the anhydride of the carbinol,

$$C_6H_4<\begin{matrix}CH{:}CH & CH{:}CH \\ NH\cdot CH\cdot O\cdot CH\cdot NH\end{matrix}>C_6H_4$$

(La Coste, Hantzsch).

It is now shown that the carbinol at first formed slowly undergoes transformation into the isomeric aldehydeamine, which is an exceedingly reactive substance. The aldehyde group can be identified by the specific colour reactions with diazobenzenesulphonic acid; corresponding derivatives are also formed with phenylhydrazine, hydroxylamine, and aniline.

The aldehydeamine combines with alcohols, forming unstable additive products, $NHR\cdot C_6H_4\cdot CH{:}CH\cdot CH(OH)\cdot OR$, from which water is eliminated, and the closed-ring alcoholates formed. It forms an additive compound with the carbinol, which, on the elimination of water, is converted into the anhydride, dihydroquinolylquinolanol.

Alkali converts the aldehyde into an oxidation product (acid) and a reduction product (alcohol), from which water is eliminated and quinolone and dihydroquinoline are formed.

Two molecules of the aldehyde undergo a benzoin condensation, forming dyes which are probably identical with the *apo*cyanines.

The aldehyde combines further with substances containing a reactionary methylene or methyl group. Water is eliminated, and dihydroquinoline derivatives, $C_6H_4<\begin{matrix}CH{:}CH \\ NR\cdot CH\cdot CHXY\end{matrix}$, are formed from the aldol intermediate product, $NHR\cdot C_6H_4\cdot CH{:}CH\cdot CH(OH)\cdot CHXY$, in addition to unsaturated substances, $NHR\cdot C_6H_4\cdot CH{:}CH\cdot CH{:}CXY$.

Both types when oxidised form dyes belonging to the class of cyanines and *apo*cyanines.

Similar transformations to the above have been observed in the *iso*quinoline and pyridine series. Thus, with *iso*quinoline the pseudo-base is transformed into the aldehyde, $CHO\cdot C_6H_4\cdot CH{:}CH\cdot NHR$, which reacts as described above. When condensed with reactive methylene compounds, dihydro*iso*quinolines are formed closely related to the alkaloids.

*iso*Quinoline and pyridine differ from quinoline in that the aldehydes tend to lose alkylamine and form nitrogen-free alcohols or the isomeric aldehydes.

The *methochloride* of the pseudo-base from 6 : 8-dinitroquinoline is obtained by heating with the theoretical quantity of methyl sulphate, dissolving the fused mass in water, and precipitating with sodium chloride; it forms brownish-yellow crystals, m. p. 203° (decomp.). Alkali hydroxides, ammonia, and sodium carbonate precipitate the pseudo-base, *dinitromethylquinolanol*, from an aqueous solution of the salt as a light yellow, indefinitely crystalline substance; it is obtained from chloroform in yellow plates, m. p. 114°. When boiled with alcohols the *alcoholates* separate in well defined crystals; the *methyl ether* has m. p. 110°; the light yellow needles of the *ethyl ether* sinter at 124°. The pseudo-base, dissolved in the nascent state in

benzene or toluene, readily separates again in light yellow flakes, which sinter at 199°, and have the composition, $C_{20}H_{16}O_9N_6$, of the anhydride, *dinitromethylquinoline oxide*; attempts to recrystallise it from ethyl alcohol result in the formation of the ethyl ether.

Dinitromethylquinolanol reacts with phenylhydrazine, forming a *phenylhydrazone*, crystallising in yellowish-brown needles, m. p. 141°. The corresponding *anil* separates in well formed, yellow needles, m. p. 186°. The evidence is insufficient to decide whether the pseudo-base has the carbinol or aldehyde structure.

On heating quinoline ethiodide, hydroxylamine hydrochloride, and potassium hydroxide, a *compound*, $C_{22}H_{25}ON_3$, crystallising in short, almost colourless needles, m. p. 214° (decomp.), was obtained, which appears to be a condensation product of two quinoline nuclei with one molecule of hydroxylamine. A red dye is also formed.

E. F. A.

Preparation of Bromo-fatty Acid Derivatives of Amino-aceto-*p*-phenetidines. CHEMISCHE WERKE VORM. DR. HEINRICH BYK (D.R.-P. 228835).—Aminoaceto-*p*-phenetidine has long been employed in pharmacy, and it is now found that its higher acyl derivatives containing bromine and an amino-residue have an enhanced therapeutic value.

*a-Bromo*iso*valerylaminoaceto-*p*-phenetidine*,

$$OEt\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot CO\cdot CHPr^{\beta}Br,$$

slender, colourless needles, m. p. 155—156°, is prepared by slowly treating a cold benzene suspension of aminoaceto-*p*-phenetidine with a molecular proportion of α-bromo*iso*valeryl bromide, allowing the mixture to remain during several hours, removing the benzene in a vacuum, and subsequent crystallisation from alcohol.

F. M. G. M.

Strongly Coloured *holo*- and *meri*-Quinonoid Imonium Salts of Benzidine and their Use for Determining the Active Value of Oxidising Agents. WALTER MADELUNG (*Ber.*, 1911, 44, 626—631).—The author does not agree with Willstätter and Kalb's view (*Ber.*, 1906, 39, 3476) that *meri*-quinonoid derivatives are deeply coloured, whereas *holo*-quinonoid compounds are yellow (compare Willstätter and Piccard, Abstr., 1908, i, 475, 915; Schlenk and Knorr, 1909, i, 36, 808).

When an aqueous solution of benzidine is oxidised with halogens, permanganate, dichromate, or iron cyanate under such conditions that the solution is kept neutral, the product is a crystalline solid with a deep cornflower-blue colour, and is very sparingly soluble. This compound probably has a constitution analogous to Schlenk's *meri*-quinonoid salt of diphenoquinonedi-imine. When further oxidised the compound deepens in colour, and gives a deep violet-coloured product, which is regarded as the *holo*-quinonoid compound. When bromine water in presence of potassium bromide is used as oxidising agent, and an amount insufficient to completely precipitate the benzidine is used, it is found that the amount of bromine required to transform the blue into the violet product is equal to the amount of bromine

required to oxidise the benzidine to the blue compound, and that the addition of more bromine water leads to the formation of a reddish-brown product, which is regarded as the quinonoid dibromoimide. When benzidine solution, or thiosulphate solution, is added to this, the change to the violet and then to the blue compound can be observed. It is suggested that Willstätter and Piccard's second chromate is in reality a *holo*-quinonoid derivative.

The salts of the *meri*- and *holo*-quinonoid compounds with mineral acids are quite stable at the ordinary temperature, but decompose when warmed and cannot be recrystallised. On addition of alkali they yield the yellow, readily soluble diphenoquinonedi-imine, which is readily decomposed by acids, for example, hydrochloric, yielding benzidine and the quinonoid dichlorobromide.

It is shown that when the blue compound formed by the action of a given amount of an oxidising agent of known concentration on benzidine is removed, acidified with hydrochloric acid, and the dichloro-imine treated with excess of potassium iodide, an amount of iodine is liberated which corresponds exactly with the oxidising value of the original volume of oxidising agent employed. The method is recommended for the estimation of small amounts of oxidising agents. As the volume of iodine solution to be titrated can be quite small compared with the volume of the original solution, it is also recommended in cases where the original solution is coloured, for example, in the case of peroxydases and blood. J. J. S.

Colloidal Form of Nastvogel's Osazone. HENRY J. H. FENTON and WILLIAM A. R. WILKS (*Proc. Camb. Phil. Soc.*, 1911, **16**, 85—86). —A colloidal solution of Nastvogel's osazone of glyoxalcarboxylic acid is obtained by boiling phenylhydrazine dihydroxymaleate with water (Trans., 1905, **87**, 808). It is readily coagulated by minute quantities of electrolytes, moves to the anode in an electric field, is not precipitated by electronegative colloids, but yields a dark brown precipitate with colloidal ferric hydroxide; in general, it behaves as a negative colloid of the suspensoid class. The most remarkable property of the colloid is its extreme sensitiveness to hydrogen ions; a solution which is unaffected by several drops of 5*N*-sodium chloride is coagulated, under similar conditions, by one drop of *N*/10-hydrochloric acid, the hydrogen ion being about 300 times as effective as the sodium ion. It is suggested that a minute quantity of some basic substance is present in the colloidal solution, and that its "protective" influence is removed on neutralisation by the acid. C. S.

Action of Hydrazine Hydrate on Ortho-diketones. THEODOR CURTIUS and RICHARD KASTNER (*J. pr. Chem.*, 1911, [ii], **83**, 215—232). —Curtius and Thun (Abstr., 1891, 1355) have shown that hydrazine hydrate reacts with ortho-diketones, such as benzil, to form derivatives of the hypothetical hydrazimethylene, $CH_2<\begin{matrix}NH\\ | \\NH\end{matrix}$. The present work has been undertaken mainly to show that *p*-tolil behaves in a similar manner.

Hydrazi-p-*tolil* (p-*toluoyl*-p-*tolylhydrazimethylene*),

$$\genfrac{}{}{0pt}{}{NH}{NH}\!\!>\!C(C_6H_4Me)\cdot CO\cdot C_6H_4Me,$$

m. p. 139—140°, is obtained by heating an alcoholic solution of *p*-tolil with hydrazine hydrate (1 mol.). It yields deoxy-*p*-toluoin when heated under reduced pressure, and in benzene solution is oxidised by yellow mercuric oxide to *azo*-p-*tolil* (p-*toluoyl*-p-*tolylazomethylene*), $\genfrac{}{}{0pt}{}{N}{N}\!\!>\!C(C_6H_4Me)\cdot CO\cdot C_6H_4Me$, m. p. 84°, red crystals, which behaves like azobenzil (Curtius and Lang, Abstr., 1892, 451), being converted by bromine in carbon tetrachloride into *dibromodeoxy*-p-*toluoin*, $C_6H_4Me\cdot CO\cdot CBr_2\cdot C_6H_4Me$, m. p. 120°. When equal molecular quantities of deoxy-*p*-toluoin and hydrazine hydrate are heated on the water-bath, *bis*-p-*toluoyl*-p-*tolylazimethylene*,

$$[C_6H_4Me\cdot CH_2\cdot C(C_6H_4Me){:}]_2N_2,$$

m. p. 155—156°, is produced.

Bishydrazi-p-*tolil* (*di*-p-*tolylbishydrazimethylene*),

$$\genfrac{}{}{0pt}{}{NH}{NH}\!\!>\!C(C_6H_4Me)\cdot C(C_6H_4Me)\!<\!\!\genfrac{}{}{0pt}{}{NH}{NH},$$

m. p. 137°, is obtained by heating *p*-tolil with a little alcohol and an excess of hydrazine hydrate at 100° for twenty-four hours; it yields 4 : 4′-dimethyltolane when its solution in benzene is treated with yellow mercuric oxide.

When a solution of hydrazibenzil in concentrated sulphuric acid is poured into water at 0°, the products obtained are benzil, benzaldehyde, benzaldazine, and bisbenzilketazine. The last substance, which is also produced by heating hydrazibenzil and benzil together at 200°, is identical with Curtius and Blumer's bisbenzoylphenylazimethylene obtained from benzoinhydrazine (Abstr., 1895, i, 600). *Bis*-p-*tolilketazine*, $N_2[{:}C(C_6H_4Me)\cdot CO\cdot C_6H_4Me]_2$, m. p. 248°, is similarly obtained from hydrazi-*p*-tolil and concentrated sulphuric acid, from hydrazi-*p*-tolil and *p*-tolil at 180°, and by heating *p*-toluoinhydrazine at 185° for five hours. (A by-product in the last reaction is *tetra*-p-*tolylpyrazine*, m. p. 287°. The corresponding by-product, $C_{28}H_{20}N_2$, obtained by Curtius and Blumer [*loc. cit.*] by heating benzoinhydrazine, is proved to be tetraphenylpyrazine, as suggested by Snape and Brooke [Trans., 1897, 71, 532].) p-*Toluoinhydrazine*,

$$C_6H_4Me\cdot CH(OH)\cdot C(C_6H_4Me){:}N\cdot NH_2,$$

m. p. 147—148°, is obtained together with tetra-*p*-tolylpyrazine by heating toluoin and hydrazine hydrate for five hours on the water-bath and keeping the mixture for three weeks before treating it with ether to remove the second product.

Bisbenzilketazine is not hydrolysed by boiling alcohol and dilute sulphuric acid or by dilute sulphuric acid at 160°, but is decomposed by the prolonged action of concentrated sulphuric acid, or rapidly by boiling aqueous alcoholic sodium hydroxide, yielding hydrazine and benzil. C. S.

Decomposition of Alloxan. ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1911, 33, 85).—Wheeler and Bogert (Abstr., 1910, i, 466)

have recorded explosions due to the decomposition of alloxan in closed bottles. The author has examined a sample of alloxan which had been kept for about a year. On the outside of the neck of the bottle was an incrustation which had evidently been forced out between the stopper and the bottle, and consisted chiefly of carbamide, oxalic acid, and alloxantin. There was considerable pressure in the bottle due to carbon dioxide, and some unaltered alloxan still remained. It is obvious, therefore, that the decomposition of alloxan takes place slowly at the ordinary temperature in accordance with certain well-known reactions. This confirms the explanation offered by Franklin (*J. Amer. Chem. Soc.*, 1910, **32**, 1362). E. G.

Constitution of Indirubin. LOUIS C. MAILLARD (*Bull. Soc. chim.*, 1911, [iv], **9**, 202—205. Compare Abstr., 1910, i, 138).—Polemical with Wahl and Bagard (this vol., i, 164). T. A. H.

Asymmetry of the Quinquevalent System Na_2bcd. MAX SCHOLTZ (*Ber.*, 1911, **44**, 480—488. Compare Abstr., 1910, i, 634).—2-Phenyl-1-*o*-xylylene-6-methylpiperidinium bromide has been shown (Abstr., 1910, i, 634) to exist in two inactive stereoisomeric modifications. Similar compounds have been prepared from *o*-xylylene bromide and coniine, conhydrine, and α-stilbazoline, all of which contain a nitrogen atom common to two rings and attached to an asymmetric carbon atom. In neither case could more than one modification be observed.

Compounds of the general formula:

$$CH_2{<}{CH_2\cdot CH_2 \atop CH_2\cdot CH_2}{>}NBr{<}{CH_2\cdot C_6H_4\cdot CH_2 \atop CH_2\cdot C_6H_4\cdot CH_2}{>}NBr{<}{CH_2\cdot CH_2 \atop CH_2\cdot CH_2}{>}CH_2$$

have been prepared by the combination of *o*-, *m*-, and *p*-xylylenedipiperidide with *o*-, *m*-, and *p*-xylylene bromide. With the exception of that from *p*-xylylenedipiperidide and *p*-xylylene bromide, they are all of the type Na_2bcd. The combination of *p*-xylylene dipiperidide with *m*-xylylene bromide yields two isomerides, one, m. p. 215°, readily soluble in alcohol, the other, m. p. 244°, which is formed in small proportion only, being sparingly soluble. The same two isomerides are formed by the combination of *m*-xylylene dipiperidide and *p*-xylylene bromide, in which case the amount of the less fusible isomeride is larger, although the more fusible form still predominates. The two dibromides also form different derivatives. They are not converted into one another on heating, and attempts to resolve them into optically active compounds were unsuccessful. They are prepared by mixing equivalent quantities of the components in chloroform solution; after twenty-four hours the condensation product has either separated as a colourless mass, or it is precipitated by ether. The bromine cannot be estimated by direct titration, but good results are obtained by the Carius' method.

p-Xylylene dipiperidide, $C_6H_4(CH_2\cdot C_5NH_{10})_2$, has m. p. 90° (compare Manoukian, Abstr., 1901, i, 528, who gives 86°). m-*Xylylene*-p-*xylylene-dipiperidinium bromide* forms a microcrystalline α-isomeride, m. p. 215°, and a granular, crystalline β-isomeride, m. p. 244°

The α-isomeride forms the following salts: *platinichloride*, m. p.

234°; *aurichloride*, m. p. 165°, decomp. above 200°; *picrate*, m. p. 161—162°, decomp. 230°. The salts of the β-isomeride are *platinichloride*, m. p. 248°; *aurichloride*, m. p. 274° (decomp.); *picrate*, darkens at 220°, but is not melted at 300°.

o-*Xylylene*-m-*xylylenedipiperidinium bromide* does not form an isomeride; it is a sandy powder, m. p. 170—173° (decomp.); the *platinichloride* has m. p. 220° (decomp.); the *picrate*, m. p. 168—170°.

o-*Xylylene*-p-*xylylenedipiperidinium bromide* has m. p. 165° (decomp.); the *platinichloride* has m. p. 225° (decomp.); the *picrate*, m. p. 143—145°.

Di-p-*xylylenedipiperidinium bromide* is not melted at 310°; the *platinichloride* decomposes at 234°; *picrate*, m. p. 241° (decomp.).

o-*Xylyleneconhydrinium bromide* was obtained as a syrup. The *platinichloride* crystallises in golden-yellow cubes and octahedra, m. p. 232° (decomp.).

o-*Xylylenestilbazolinium bromide* is also a syrup; the *platinichloride* has m. p. 132°.

It was shown previously (Abstr., 1901, 483) that 2 : 6-diphenylpiperidine exists in two inactive forms. One of these, m. p. 71°, reacts with ethyl iodide and sodium hydroxide to form 2 : 6-*diphenyl*-1-*ethylpiperidine*, which crystallises in long, lustrous needles, m. p. 83°. It reacts with benzoyl iodide, one modification only of 2 : 6-*diphenyl*-1-*benzyl*-1-*ethylpiperidinium iodide*,

$$CH_2{<}{\substack{CH_2\cdot CHPh\\ CH_2\cdot CHPh}}{>}NIEt\cdot C_7H_7,$$

being obtained; this crystallises in colourless needles, m. p. 261°. Accordingly, 2 : 6-diphenylpiperidine, m. p. 71°, corresponds with the mesotartaric type, and cannot be resolved. E. F. A.

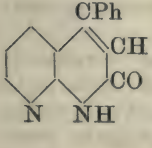
Syntheses of Derivatives of 1 : 8-Naphthyridine from α-Aminopyridine. F. Carlo Palazzo and Astorre Tamburini (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 37—44).—By heating α-aminopyridine with ethyl acetoacetate for an hour and a-half in a sealed tube at 120—125°, *α-acetoacetylaminopyridine*,

$$C_5H_4N\cdot NH\cdot CO\cdot CH{:}CMe\cdot OH,$$

is obtained. It crystallises in colourless needles, m. p. 113° (softening towards 110°), is soluble in acids and alkalis, gives a green precipitate with ammoniacal copper acetate, and an intense reddish-violet coloration with ferric chloride. *α-Benzoacetylaminopyridine*,

$$C_5NH_4\cdot NH\cdot CO\cdot CH{:}CPh\cdot OH,$$

similarly prepared, crystallises in colourless needles, m. p. 110° (softening at 106°), and has properties similar to those of the acetoacetyl derivative. When heated for twenty to twenty-five minutes at 100° with concentrated sulphuric acid, it condenses to 4-*phenyl*-1 : 8-*naphthyrid*-2-*one* (annexed formula), which can be obtained on neutralising the solution, and forms colourless, silky needles, m. p. 150° (previously softening). The substance has only basic properties; it dissolves in acids, and is reprecipitated by alkals. It yields a *platinichloride*. It gives no coloration with ferric chloride. Acetoacetylaminopyridine behaves with



concentrated sulphuric acid like the benzoyl derivative, but for lack of substance the analogous naphthyridine could not be isolated.

R. V. S.

Quinoline Dyes. I. *apo*Cyanines. ADOLF KAUFMANN and PAUL STRÜBIN [and, in part, A. ANASTACHEWITCH, N. POPPER, and L. SZNAJDER] (*Ber.*, 1911, **44**, 690—701).—By the action of alkali on the quaternary salts of quinoline, particularly on warming, red to black dyes are formed, together with resins, in a manner analogous to the well-known cyanines and *iso*cyanines. The name *apo*cyanine is suggested for the new dyes, and distinction is made between the red *erythro*apo*cyanines* and the more yellow *xantho*apo*cyanines*, which are formed side by side. They are characterised by the fact that their aqueous solutions are not instantaneously decolorised by mineral acids.

When quinoline ethiodide is boiled with potassium hydroxide in methyl alcohol, the solution changes from yellow to red, then becomes reddish-violet, and yellow crystals of the *xantho*apo*cyanine* separate. These are separated by filtration, and, after a time, red needles of coppery lustre of the *erythro*apo*cyanine* crystallise, the proportion of the red dye being considerably greater than that of the yellow dye.

*Erythro*apo*cyanine*, $C_{22}H_{23}N_2I$, decomposes at 210—220°; the *nitrate* crystallises in dark red prisms, m. p. 169—170°. The homologous *dimethylerythro*apo*cyanine hydriodide* forms deep red, lustrous needles, m. p. 238° (decomp.).

The erythro*apo*cyanines are probably the monoacid salts of 2 : 2-diquinolenyls; they have weak basic properties. The neutral colourless salts are dissociated on dilution with water, and form the coloured basic salts. Oxidising agents destroy the double bond between the two quinoline nuclei, which appears to be the carrier of the chromophoric properties, with the formation of 2 : 2-diquinolyl derivatives.

Thus the *diethyl picrate* of a *diquinolyl*, $C_{34}H_{26}O_{14}N_8$, is obtained in slender, yellow needles, m. p. 186°, by the action of picric acid on diethyl-2 : 2-diquinolenyl hydriodide. At the same time, a more soluble red substance, m. p. 162°, is obtained, which is converted into the above picrate on oxidation; it possibly represents a neutral picrate of diquinolen. *Diethyldiquinolyl chromate* forms yellowish-red needles, and becomes black at 190°, m. p. 210° (decomp.).

2 : 2-*Diquinolyl diethiodide*, prepared by the action of iodine on diethyldiquinolenyl hydriodide, crystallises in long, citron-yellow needles, m. p. 198°. It yields the dipicrate described above. A second iodo-derivative, the *periodide*, $C_{22}H_{22}N_2I_7$, is formed in smaller quantity; it is a dark brownish-red, crystalline powder, m. p. 152° (decomp.).

A similar *perbromide*, $C_{22}H_{22}N_2IBr_6$, crystallises in lustrous, golden-yellow plates, m. p. 197—199°.

Diethyldiquinolenyl hydriodide was converted into the corresponding *chloride*, which is more soluble, and oxidised with cold alkaline potassium ferricyanide; the *oxidation product*, $C_{22}H_{20}O_2N_2$, forms slender, colourless needles, m. p. 176°. It has faintly basic

properties and forms a *platinichloride*, m. p. 196—197°, which readily dissociates.

The corresponding product from dimethyldiquinolenyl hydrochloride forms yellow, rhombic crystals, m. p. 243°.

The xantho*apo*cyanines are more sparingly soluble, melt above 300°, have a yellowish-green fluorescence in solution, and are more stable towards mineral acids. They are not oxidised by iodine or potassium ferrocyanide.

The orange-yellow dye, $C_{22}H_{23}N_2I$, from quinoline ethiodide, crystallises in long, matted needles, m. p. 320° (decomp.); the corresponding yellow dye from quinoline methiodide crystallises in needles, m. p. above 300°. The *nitrate* separates in orange-yellow needles, which are partly decomposed on drying at 120°. The xantho*apo*cyanines have no basic properties; alkalis precipitate almost colourless bases, which rapidly change, have no definite melting point, and are characterised by the blue fluorescence when dissolved in alcohol or concentrated sulphuric acid. E. F. A.

Tri-indylmethane Dyes. ALEXANDER ELLINGER and CLAUDE FLAMAND (*Zeitsch. physiol. Chem.*, 1911, 71, 7—13. Compare Abstr., 1909, i, 846).—The dye obtained, as *sulphate*, on heating 2-methylindole-3-aldehyde with dilute sulphuric acid, whereby formic acid is formed, crystallises in long, reddish-violet needles, which sinter at 175°, m. p. 212° (decomp.). By treatment with ammonia, the *dye*, $C_{28}H_{23}N_3$, is obtained as bright yellow, narrow plates, m. p. 234—237°. The dye is even more readily formed in the cold from 2-methylindole, formic acid, and 20% sulphuric acid. It is also obtained by the condensation of methylindolealdehyde and methylindole in concentrated alcoholic solution with the addition of two drops of concentrated hydrochloric acid. On boiling with water at 230° under pressure, it is hydrolysed to these two components. The *leuco*-compound, $C_{28}H_{25}N_3$, is formed along with the dye by the last-described method; it has a faint rose tint, m. p. 319°. E. F. A.

Reactions of 1-Chloro-2 : 6-dinitrobenzene. WALTHER BORSCHE and D. RANTSCHEFF (*Annalen*, 1911, 379, 152—182. Compare Abstr., 1909, i, 232).—The product described by Jungfleisch (*Jahresb.*, 1868, 345) as 1-chloro-2 : 6-dinitrobenzene is shown to be a mixture of 25% of this compound with 75% of the 2 : 4-dinitro-compound, and this accounts for the statement that the 2 : 6-compound is transformed into the 2 : 4- when impregnated with a crystal of the latter.

The separation of the two isomeric dinitro-derivatives is accomplished most readily by means of ethyl sodioacetoacetate, which reacts with the 2 : 4-compound much more readily than with the isomeride. The ethereal solution of the chloro-2 : 6-dinitrobenzene and the ethyl 2 : 4-dinitrophenylacetoacetate is extracted with water and then 2% sodium hydroxide solution, which removes the ester. 1-*Chloro-2 : 6-dinitrobenzene*, $C_6H_3Cl(NO_2)_2$, crystallises from alcohol in slender, yellow needles, m. p. 92°, and when finely divided has an irritating action on the mucous membrane. Its constitution has been proved by

conversion into 2 : 6-dinitrophenol, 2 : 6-dinitrophenetole, and 2 : 6-dinitroaniline. The atom of chlorine is reactive, and can be replaced by various types of substituents.

2 : 6-*Dinitrophenyl ether*, $OPh\cdot C_6H_3(NO_2)_2$, prepared from sodium phenoxide and 1-chloro-2 : 6-dinitrobenzene, crystallises from alcohol in colourless plates, m. p. 99—100°. When reduced with an alcoholic solution of ammonium sulphide, the chloro-derivative yields *m*-nitroaniline, but with stannous chloride solution yields 2-chloro-*m*-phenylenediamine, $C_6H_7N_2Cl$, m. p. 85—86°, which forms a *dibenzoyl* derivative, $C_{20}H_{15}O_2N_2Cl$, m. p. 196—197°.

3-*Nitro*-o-*phenylenediamine*, $NO_2\cdot C_6H_3(NH_2)_2$, obtained by reducing 2 : 6-dinitroaniline with an alcoholic solution of ammonium sulphide, crystallises from dilute alcohol in dark red needles, m. p. 158—159°, and in the presence of pyridine yields a benzoyl derivative, $C_{13}H_{11}O_3N_3$, in the form of dark yellow, refractive needles, m. p. 206°.

4-*Nitro-2-methylbenziminazole*, $NO_2\cdot C_6H_3<{}^{N}_{NH}>CMe$, is formed when the nitro-*o*-phenylenediamine is boiled for several hours with acetic anhydride, and crystallises from dilute alcohol in compact, yellow needles, m. p. 217°. o-*Nitro*-1 : 2 : 3-*benztriazole*,

$$NO_2\cdot C_6H_3<{}^{N}_{NH}>N,$$

obtained by dissolving nitro-*o*-phenylenediamine in hydrochloric acid and treating with sodium nitrite solution, crystallises from alcohol in compact, glistening, brown needles, which decompose at 230°. The *o*-diamine also condenses with α-diketones; for example, when boiled with an alcoholic solution of benzil for several hours it yields 5-*nitro*-2 : 3-*diphenylquinoxaline*, $NO_2\cdot C_6H_3<{}^{N:CPh}_{N:CPh}$, which crystallises from a mixture of alcohol and chloroform, and has m. p. 169—170°. Its solution in concentrated sulphuric acid has a blood-red colour.

2 : 6-*Dinitrodimethylaniline*, $NMe_2\cdot C_6H_3(NO_2)_2$, obtained by the action of a 33% aqueous solution of dimethylamine on an alcoholic solution of 2 : 6-dinitrochlorobenzene, crystallises from dilute alcohol in slender orange-yellow needles, m. p. 78°, and when reduced with alcoholic ammonium sulphide yields 3-*nitro*-o-*phenylenedimethyldiamine*, $NO_2\cdot C_6H_3(NH_2)(NMe_2)$, as a dark red pasty mass. The corresponding *benzoyl* derivative, $C_{15}H_{15}O_3N_3$, crystallises in yellow needles, m. p. 114°.

Piperidine and chloro-2 : 6-dinitrobenzene in alcoholic solution yield 1-*di*-o-*nitrophenylpiperidine*, $C_6H_3(NO_2)_2\cdot N<{}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>CH_2$, which crystallises in long, brittle, yellow needles, m. p. 106—107°.

2 : 6-*Dinitrodiphenylamine*, $C_6H_3(NO_2)_2\cdot NHPh$, is formed when chloro-2 : 6-dinitrobenzene is boiled for several hours with an alcoholic solution of aniline and sodium acetate, and crystallises from alcohol in brilliant orange-red plates, m. p. 107—108°. An 80% yield of the corresponding 6-*nitro-2-aminodiphenylamine*, $C_{12}H_{11}O_2N_3$, is obtained by reducing the dinitro-compound with ammonium sulphide; it crystallises from alcohol in black prisms with a green

reflex, has m. p. 101°, and when finely divided has a dark red colour. With nitrous acid it yields 7-*nitro*-1-*phenyl*-1 : 2 : 3-*benztriazole*,

$$NO_2\cdot C_6H_3<\begin{matrix}—N\\ NPh\end{matrix}>N,$$

in the form of pale yellow needles, m. p. 152—153°. This latter does not yield a nitrocarbazole when heated (compare Ullmann, Abstr., 1904, i, 776), but when reduced with stannous chloride and concentrated hydrochloric acid in the presence of alcohol yields a mixture of 4-*chloro*-7-*amino*-1-*phenyl*-1 : 2 : 3-*benztriazole* and 7-*amino*-1-*phenyl*-1 : 2 : 3-*benztriazole.* The former crystallises from hot alcohol in pale green needles, m. p. 211°, but the latter could not be obtained in a pure form.

2 : 6-*Diaminodiphenylamine*, $C_6H_3(NH_2)_2\cdot NHPh$, obtained by reducing the dinitro-derivative with iron and dilute hydrochloric acid, crystallises from a mixture of ether and light petroleum in colourless prisms, which turn brown on exposure to the air and have m. p. 178°.

2 : 6-*Dinitrophenylhydrazine*, $C_6H_3(NO_2)_2\cdot NH\cdot NH_2$, crystallises from dilute alcohol in red needles, m. p. 144—145°; the *hydrochloride* crystallises from hot water in brilliant red needles, and with excess of alkali yields salts of 7-nitrobenztriazole, from which the triazole can be obtained by the action of nitric acid.

7-*Nitro*-1-*hydroxybenztriazole*, $NO_2\cdot C_6H_3<\begin{matrix}—N\\ N(OH)\end{matrix}>N$, crystallises from hot water or dilute alcohol in orange-coloured needles, containing $1H_2O$, and decomposing with violence at 229°. 2 : 6-Dinitrophenylhydrazine condenses with quinones and quinoneoximes in the presence of dilute hydrochloric acid in much the same manner as the isomeric 2 : 4-dinitro-compound (Abstr., 1908, i, 66).

2 : 6-*Dinitro*-4′-*hydroxyazobenzene*, $C_6H_3(NO_2)\cdot N:N\cdot C_6H_4\cdot OH$, crystallises from dilute alcohol in brownish-yellow needles, m. p. 172°. p-*Benzoquinoneoxime*-2 : 6-*dinitrophenylhydrazone*,

$$C_6H_3(NO_2)_2\cdot NH\cdot N:C_6H_4:N\cdot OH,$$

forms a brown, crystalline powder decomposing at 230°; it is readily transformed by dilute sodium hydroxide solution into 4 : 4′-*di*(2 : 6-*dinitrobenzeneazo*)-*azoxybenzene*, $ON_2[C_6H_4\cdot N:N\cdot C_6H_3(NO_2)_2]_2$, m. p. 255—256°, and is oxidised by a mixture of glacial acetic and nitric acids to 2 : 6 : 4′-*trinitroazobenzene*, $C_6H_3(NO_2)_2\cdot N_2\cdot C_6H_4\cdot NO_2$, which crystallises in slender, reddish-yellow needles, m. p. 168°.

4-*Nitro*-2-*phenyl*-2 : 1 : 3-*benztriazole*, $NO_2\cdot C_6H_3<\begin{matrix}N\\ |\\ N\end{matrix}>NPh$, obtained by heating an alcoholic solution of chloro-2 : 6-dinitrobenzene and phenylhydrazine with sodium acetate, crystallises from alcohol in glistening, yellow needles, m. p. 160°. 2 : 6-*Dinitrophenylpyridonium chloride*, $C_6H_3(NO_2)_2\cdot C_5NH_5Cl$, crystallises from alcohol in nearly colourless needles, m. p. 201°.

A small amount of 2 : 6 : 2′ : 6′-*tetranitrodiphenyl*, $C_{12}H_6(NO_2)_4$, is formed when chloro-2 : 6-dinitrobenzene is heated with nitrobenzene and copper powder (compare Ullmann and Bielecki, Abstr., 1901, i, 586) It crystallises from glacial acetic acid in slender, yellow needles, m. p. 217—218°. The chief by-product is 2 : 6-dinitrodiphenylamine.

1-Chloro-2 : 6-dinitrobenzene does not react so readily with ethyl sodioacetoacetate as the 2 : 4-isomeride, and in order to complete the reaction, the mixture must be heated for about four days. *Ethyl* 2 : 6-*dinitrophenylacetoacetate*, $C_{12}H_{12}O_7N_2$, crystallises from alcohol in compact, yellow needles, m. p. 90°. Its O-*benzoyl* derivative, $C_{19}H_{16}O_8N_2$, also forms yellow crystals, m. p. 130—131°, and when dissolved in concentrated sulphuric acid and diluted with water, yields 2 : 6-dinitrobenzyl methyl ketone. The ester does not react with ammonia, aniline, or phenylhydrazine, but when reduced with stannous chloride yields *ethyl* 4-*amino*-2-*methylindole*-3-*carboxylate*,

$$NH_2{\cdot}C_6H_4{<}{\begin{matrix}C(CO_2Et)\\NH\end{matrix}}{>}CMe.$$

This crystallises from alcohol in colourless plates, m. p. 148°, which turn brown on exposure to the air. 2 : 6-*Dinitrobenzyl methyl ketone*, $C_6H_3(NO_2)_2{\cdot}CH_2{\cdot}COMe$, crystallises from alcohol in yellow needles, m. p. 106—107°. It does not react with diazonium salts, but forms a *phenylhydrazone*, $C_{15}H_{14}O_4N_4$, in the form of orange-red needles, m. p. 112°, which dissolve in alkalis, yielding deep blue solutions. When reduced with alcoholic ammonium sulphide, the ketone yields 4-*nitro*-1-*hydroxy*-2-*methylindole*, $NO_2{\cdot}C_6H_3{<}{\begin{matrix}CH\\N(OH)\end{matrix}}{>}CMe$, as orange-red needles, m. p. 186—187°, which react with sodium methoxide and methyl iodide, yielding the *methyl ether*, $C_{10}H_{10}O_3N_2$, in the form of greenish-yellow needles, m. p. 91—92°.

Ethyl 2 : 6-*dinitrophenylmalonate*, $C_{13}N_{14}O_8N_2$, crystallises from alcohol in compact, yellow needles, m. p. 54—55°, and when hydrolysed with acetic and sulphuric acids yields 2 : 6-*dinitrophenylacetic acid*, $C_6H_3(NO_2)_2{\cdot}CH_2{\cdot}CO_2H$, which crystallises from glacial acetic acid in yellow plates, m. p. 201—202° (decomp.). The *methyl* ester,

$$C_9H_8O_6N_2,$$

has m. p. 57°, and reacts with salicylaldehyde and a few drops of piperidine at 150°, yielding 2 : 6-*dinitrophenylcoumarin*,

$$C_6H_4{<}{\begin{matrix}CH{:}C{\cdot}C_6H_3(NO_2)_2\\O\text{---}CO\end{matrix}},$$

as a yellow, crystalline powder, m. p. 233—234°.

1-Chloro-2 : 4-dinitrobenzene reacts with an alcoholic solution of potassium xanthate, yielding Beilstein and Kurbatoff's 2 : 4-dinitrophenyl sulphide (*Annalen*, 1879, **197**, 77). The 2 : 6-isomeride does not react in a similar manner.

2 : 4-*Dinitrophenyl*-o-*phenylenediamine*, $C_{12}H_{10}O_4N_4$, obtained by the action of an alcoholic solution of *o*-phenylenediamine on chloro-2 : 4-dinitrobenzene, crystallises from alcohol in orange needles, m. p. 150—151°. The *hydrochloride* crystallises in brilliant, yellow plates and reacts with nitrous acid, yielding 1-o:p-*dinitrophenyl*-1 : 2 : 3-*benztriazole*, $C_6H_4{<}{\begin{matrix}N[C_6H_3(NO_2)_2]\\N{:}N\end{matrix}}{>}$, which crystallises from glacial acetic acid in broad, yellow needles, m. p. 186—187°, but cannot be transformed into a carbazole derivative. J. J. S.

Action of Amidines on Cyanoguanidine. ADRIANO OSTROGOVICH (*Atti R. Accad Lincei*, 1911, [v], **20**, i, 182—186).—When a

mixture of cyanoguanidine and acetamidine hydrochloride is gradually heated to 230°, and the temperature maintained at that point for a short time, ammonia is evolved, and on dissolving the reaction product in dilute hydrochloric acid, 4 : 6-diamino-2-methyl-1 : 3 : 5-triazine dihydrochloride (Ostrogovich, *Chem. Zentr.*, 1905, ii, 1360) is obtained. The yield is 65—70% of the theoretical, so that the method is convenient for the preparation of this substance. From benzamidine, 4 : 6-*diamino-2-phenyl*-1 : 3 : 5-*triazine* is similarly obtained in about the same yield. It crystallises in small, colourless needles, m. p. 225°, and is identical with the benzoguanamine of Elzanowski (*Diss.*, Freiburg [Switzerland], 1898). It gives a *platinichloride*, which crystallises in pale yellow needles, a *dichromate*, which forms orange-red needles, and a *hydrochloride*, $C_9H_9N_5,HCl,H_2O$, crystallising in lustrous, prismatic needles. The *picrate*, $C_9H_9N_5,C_6H_3O_7N_3$, forms yellow needles, m. p. 255—256°. R. V. S.

Substituted Rhodanic Acids and their Condensation Products with Aldehydes and Ketonic Substances. XI. EGON BUTSCHER (*Monatsh.*, 1911, **32**, 9—19).—Hitherto only the condensation products of substituted rhodanic acids with aromatic aldehydes and with furfuraldehyde have been described. The following substances have now been prepared: 5-*Valerylidene-3-phenylrhodanic acid*, $CHMe_2\cdot CH_2\cdot CH:C<\begin{matrix}S-CS\\ CO\cdot NPh\end{matrix}$, m. p. 113°, yellow needles, is obtained by heating 3-phenylrhodanic acid and valeraldehyde for two hours in glacial acetic acid. The following compounds have been prepared in a similar manner from alloxan and the substituted rhodanic acids: 5-*Alloxan-3-phenylrhodanic acid*, $R:C<\begin{matrix}S-CS\\ CO\cdot NPh\end{matrix}$ (where R =

$$CO<\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}>C:),$$

decomp. 270—280°, yellow needles. 5-*Alloxan-3-allylrhodanic acid*, $R:C<\begin{matrix}S-CS\\ CO\cdot N\cdot C_3H_5\end{matrix}$, m. p. 166° (decomp.), yellow leaflets. 5-*Alloxan-3-methylrhodanic acid*, $C_8H_5O_4N_3S_2$, decomp. 220—225°, yellow needles. 5-*Alloxan*-3-p-*tolylrhodanic acid*, $C_{14}H_9O_4N_3S_2$, m. p. 270° (decomp.), microscopic, yellow needles. 5 : 5′-*Phenanthrenebis-3-phenylrhodanic acid*, $\begin{matrix}CS-S\\ NPh\cdot CO\end{matrix}>C:\overset{C_6H_4\cdot C_6H_4}{C-\!\!-\!\!-C}=C<\begin{matrix}S-CS\\ CO\cdot NPh\end{matrix}$, m. p. 291—292°, is obtained from phenanthraquinone and 3-phenylrhodanic acid (2 mols.) in hot glacial acetic acid; a *substance*, $C_{24}H_{18}O_2N_2S_4$, m. p. 216—218°, of similar constitution is obtained from 3-ethylrhodanic acid.

When 5-*p*-methoxybenzylidene-3-phenylrhodanic acid is hydrolysed by boiling baryta, the expected α-thiol-*p*-methoxycinnamic acid is obtained in the form of the corresponding *disulphide*,

$$[OMe\cdot C_6H_4\cdot CH:C(CO_2H)]_2S_2,$$

m. p. 202—203°. In another experiment in which the hydrolysis was effected by alcoholic potassium hydroxide, the mercaptan was

isolated as its *benzyl* derivative,

$$OMe\cdot C_6H_4\cdot CH:C(CO_2H)\cdot S\cdot C_7H_7,$$

m. p. 131—134°. C. S.

Intramolecular Changes. MAX BUSCH and OTTO LIMPACH (*Ber.*, 1911, **44**, 560—583).—Of the two isomeric substances obtained by the interaction of carbonyl chloride and $\beta\delta$-diphenylthiosemicarbazide (Marckwald and Sedlaczek (Abstr., 1896, i, 231), the labile, more fusible compound was shown by Busch, Reinhardt, and Limpach (Abstr., 1910, i, 142) to be 5-thio-*n*-1 : 4-diphenylurazole, and the stable isomeride to be 5-thiol-1 : 4-diphenyl*endo*oxydihydrotriazole. The latter still retains its constitution, but the labile compound, which is more conveniently obtained by the action of an excess of 20% carbonyl chloride in toluene on a benzene solution of $\beta\delta$-diphenylthiosemicarbazide at 60—70° (the two isomerides are separated as described, *loc. cit.*), is proved to be 3-*phenyl*-1 : 3 : 4-*thiodiazole*-5-*one*-2-*anil*,

$$NPh:C{<}\begin{matrix}S\text{——}CO\\ \quad | \\ NPh\cdot NH\end{matrix},$$

by the evidence quoted below. It reacts with phenylhydrazine or primary bases, yielding two products, one of which does not contain sulphur. Thus, with aniline on the water-bath, $a\delta$-diphenylsemicarbazide and thiocarbanilide are formed, whilst with phenylhydrazine (2 mols.) the labile compound yields $a\delta$-diphenylthiosemicarbazide and diphenylcarbazide. This facile fission of the ring suggests that the labile compound cannot be a urazole derivative, since true urazoles, such as 1-phenylurazole, 1 : 4-diphenylurazole, and 1 : 4-diphenyl-2-methylurazole, are stable to aniline or phenylhydrazine even at 150°. (5-Triol-1 : 4-diphenyl*endo*oxydihydrotriazole, the stable isomeride, is not attacked by boiling aniline.)

The key to the constitution of the labile compound is obtained by the behaviour of the substance on methylation. When heated with methyl iodide, it yields methyl mercaptan and 1 : 4-diphenyl-2-methylurazole, amongst other products. When kept overnight in contact with an excess of methyl sulphate, however, it yields two products, neither of which contains the group ·SMe. The by-product, m. p. 77—78°, is 5-*methoxy*-3-*phenyl*-1 : 3 : 4-*thiodiazole*-2-*anil*, $NPh:C{<}\begin{matrix}S\text{——}C\cdot OMe\\ \quad \| \\ NPh\cdot N\end{matrix}$, has basic properties, gives a quantitative yield of methyl iodide by Zeisel's method, and is probably identical with the methyl compound, m. p. 74·5—75·5°, obtained by Nirdlinger and Acree (Abstr., 1910, i, 785). The chief product of the methylation has m. p. 92°, is decomposed profoundly by hydriodic acid, and reacts with primary bases even more vigorously than its parent substance. It is decomposed by boiling 8% alcoholic potassium hydroxide, yielding $\beta\delta$-*diphenyl*-a-*methylthiosemicarbazide*, $NHMe\cdot NPh\cdot CS\cdot NHPh$, m. p. 138°, which is transformed at 150° into the β-isomeride, $NHPh\cdot NMe\cdot CS\cdot NHPh$, m. p. 176—177°, obtained by Marckwald. The formation of $\beta\delta$-diphenyl-a-methylthiosemicarbazide from the methylated product, m. p. 92°, proves that the latter must be either $NPh:C{<}\begin{matrix}S\text{——}CO\\ \quad | \\ NPh\cdot NMe\end{matrix}$ or

$SC<\begin{matrix}NPh\cdot NMe\\ \vert\\ NPh\cdot CO\end{matrix}$. The latter constitution does not harmonise with the pronounced basic character of the substance, whilst the former is supported by the formation of the compound from carbonyl chloride and $\beta\delta$-diphenyl-α-methylthiosemicarbazide in benzene at 50—60°. The proof that the substance, m. p. 92°, has the former constitution is obtained by carefully heating the compound with alcoholic ammonia or potassium hydroxide; by this means it is converted into an *isomeride*, m. p. 165°, which has no basic properties and is easily desulphurised by mercuric oxide and benzene at 140—150°, yielding 1 : 4-diphenyl-2-methylurazole. Consequently the isomeride, m. p. 165°, has the latter of the two constitutions given above, the methylated product, m. p. 92°, has the former constitution, and, finally, therefore, the parent substance, the labile compound, formerly regarded as 1 : 4-diphenyl-5-thiourazole, must be 3-phenyl-1 : 3 : 4-thiodiazolone-2-anil, as mentioned above.

1 : 4-Diphenyl-2-methylurazole is conveniently obtained by warming 5-thiol-1 : 4-diphenyl*endo*oxydihydrotriazole with an excess of methyl sulphate and treating the product, still in the presence of methyl sulphate, with dilute sodium hydroxide; by the elimination of methyl mercaptan and the simultaneous entrance of a methyl group, 1 : 4-diphenyl-2-methylurazole is formed, together with a small quantity of 3-*methoxy*-1 : 4-*diphenyl*-1 : 2 : 4-*triazolone*, $NPh<\begin{matrix}CO\text{———}NPh\\ \vert\\ C(OMe):N\end{matrix}$, m. p. 110—111°. The latter is stable to alcoholic alkalis, whilst 1 : 4-diphenyl-2-methylurazole is converted by 10% alcoholic potassium hydroxide into a mixture of approximately equal quantities of $\alpha\delta$-*diphenyl*-β-*methylsemicarbazide*, $NHPh\cdot CO\cdot NMe\cdot NHPh$, m. p. 138° (which, like other members of the β-series, does not possess basic properties), and $\beta\delta$-*diphenyl*-α-*methylsemicarbazide*,

$$NHPh\cdot CO\cdot NPh\cdot NHMe,$$

m. p. 140°. The attempt to prepare 5-thio-1 : 4-diphenyl-2-methylurazole from either of these compounds and thiophosphoryl chloride failed altogether with the β-compound. $\beta\delta$-Diphenyl-α-methylsemicarbazide and thiophosphoryl chloride in benzene solution, however, yield the *thiocarbonyl chloride*, $NHPh\cdot CO\cdot NPh\cdot NMe\cdot CS\cdot Cl$, which loses hydrogen chloride at its m. p., 150°, and forms 3-*thion*-1 : 4-*diphenyl*-2-*methylurazole*, $NPh<\begin{matrix}CS\cdot NMe\\ \vert\\ CO\cdot NPh\end{matrix}$, m. p. 165·5°. This substance, which yields 1 : 4-diphenyl-2-methylurazole by desulphurisation by mercuric oxide and alcohol, is also obtained by the action of alcoholic ammonia on 3-*phenyl*-4-*methyl*-1 : 3 : 4-*thiodiazolone*-5-*anil*, $NPh:C<\begin{matrix}NMe\cdot NPh\\ \vert\\ S\text{———}CO\end{matrix}$, m. p. 102°, prepared by the interaction of carbonyl chloride and $\alpha\delta$-diphenyl-β-methylthiosemicarbazide in the same manner as 3-phenylthiodiazolone-5-anil from carbonyl chloride and $\beta\delta$-diphenylthiosemicarbazide.

The preceding facts leave no doubt as to the course of the reaction between carbonyl chloride and $\beta\delta$-dialkylthiosemicarbazides. The

labile compound first formed is a thiodiazoloneanil,

$$\begin{matrix} RN\cdot NH_2 \\ RN{:}C\cdot SH \end{matrix} + COCl_2 \longrightarrow \begin{matrix} R\cdot N\cdot NH \\ RN{:}C\text{——}S \end{matrix}\!\!>CO,$$

which is easily converted (by fusion or in alcoholic solution) into the stable thiol*endo*oxydihydrotriazole (annexed formula), the thiourazole, $\begin{matrix} RN\cdot NH \\ SC-NR \end{matrix}\!\!>CO$, being an intermediate product. By desulphurisation the thiol*endo*oxydihydrotriazole regenerates the urazole ring,

$$\begin{matrix} RN\text{————}N \\ SH\cdot C{<}^{-O-}_{NR}{>}C \end{matrix}$$

$$\begin{matrix} RN-N \\ OC\cdot NR \end{matrix}\!\!>C\cdot OH \text{ or } \begin{matrix} RN\cdot NH \\ OC\cdot NR \end{matrix}\!\!>CO.$$

The authors deny that the interconversion of the salts of 5-thiol-1 : 4-diphenylurazole (*endo*oxy-5-thiol-1 : 4-diphenyldihydrotriazole) and 5-thion-1 : 4-diphenylurazole (3-phenyl-1 : 3 : 4-thiodiazolone-5-anil) is a reversible process, as stated by Nirdlinger and Acree (*loc. cit.*); they show that the change only proceeds in the direction, thiodiazolone $\longrightarrow$ thioltriazole, and in aqueous solution is completed in twelve hours at 100° and in thirty-six hours at 80°. C. S.

Derivatives of Hydrazodicarbonamide and of Urazole. GUIDO PELLIZZARI (*Gazzetta*, 1911, 41, i. 30—38. Compare Abstr., 1907, i, 874).—[With L. ACCAME.]—From aminophenylcarbamide and potassium cyanate in aqueous solution in the presence of acetic acid, *phenylhydrazodicarbonamide*, $NH_2\cdot CO\cdot NPh\cdot NH\cdot CO\cdot NH_2$, is obtained as a colourless, crystalline precipitate, m. p. 221° (decomp.). When heated at its melting point the compound yields phenylurazole. The preparation of *phenylhydrazo-β-thiodicarbonamide*,

$$NH_2\cdot CO\cdot NPh\cdot NH\cdot CS\cdot NH_2,$$

is effected by mixing in alcoholic solution aminophenylcarbamide, hydrochloric acid, and ammonium thiocyanate. The precipitate of ammonium chloride is filtered off, and the liquid is boiled for three hours. The precipitate so obtained forms after recrystallisation colourless crystals, m. p. 235° (decomp.).

[With A. LARIA-BOTTE.]—*Phenylhydrazo-a-thiodicarbonamide*,

$$NH_2\cdot CS\cdot NPh\cdot NH\cdot CO\cdot NH_2,$$

is prepared from aminophenylthiocarbamide and potassium cyanate in the presence of hydrochloric acid, and forms lustrous crystals, m. p. 213° (decomp.). A sample when heated began to evolve ammonia at 190°, and the evolution increased at 210°, at which temperature the substance was maintained for half an hour. From the product obtained on cooling, 1-*phenyl*-5-*thiourazole*, $NPh{<}\begin{matrix} NH\cdot CO \\ CS-NH \end{matrix}$, was isolated. It forms very small, yellowish-white crystals, m. p. 227—230°. Attempts to obtain the substance from carbamide and aminophenylthiocarbamide yielded only resinous products.

When aminophenylthiocarbamide is boiled in alcoholic solution for several hours, it is transformed into phenylsemithiocarbazide. The change can be explained on the lines of the well-known transformations of carbamide and thiocarbamide on heating.

The preparation of a salt of aminophenylguanidine is more easily

effected by the interaction of cyanamide and phenylhydrazine hydrobromide than by the method formerly given (Abstr., 1897, i, 47), because the hydrobromides of the two products can be separated by crystallisation. Phenylaminoguanidine *hydrobromide* is recrystallised from water containing hydrobromic acid, and forms slightly coloured, small needles, m. p. 210°. Aminophenylguanidine *hydrobromide* crystallises in hexagonal tablets, m. p. 219°, and is more soluble in water than its isomeride, but less soluble in alcohol.

From aminophenylguanidine hydrobromide and potassium cyanate or thiocyanate no product could be prepared, and even with cyanamide the introduction of a second guanidine group could not be effected. When aminophenylguanidine hydrobromide and carbamide are heated together at 200° for half an hour, however, 5-*imino*-1-*phenylurazole*, $NPh<\begin{matrix}NH\text{---}CO\\ C(:NH)\cdot NH\end{matrix}$, is obtained. It forms long, lustrous needles, m. p. 272—273° (decomp.), and is soluble in ammonia. From this solution it is precipitated by acetic acid, but it is soluble in dilute hydrochloric acid. From the mother liquors from its preparation a *substance*, m. p. towards 235—240°, was also isolated. R. V. S.

Condensations of Hydrazoic Acid with Cyanoformic Ester and with Cyanogen Bromide. III. E. OLIVERI-MANDALÀ (*Gazzetta*, 1911, 41, i, 59—63. Compare Abstr., 1910, i, 593).—Ethyl cyanoformate and a concentrated ethereal solution of hydrazoic acid when heated together under pressure for several days at 50° yield in small quantity ethyl tetrazolecarboxylate, $CN_4H\cdot CO_2Et$, which crystallises in small needles, m. p. 85—86° (previously softening). The substance has an acid reaction. When it is warmed with alcoholic potassium hydroxide, a substance is deposited, probably the potassium salt, which on addition of acid forms tetrazole.

Cyanogen bromide and hydrazoic acid under similar conditions yield bromotetrazole, CN_4HBr, also in small amount. The substance after previously softening has m. p. 147—148° (decomp.). It has a strongly acid reaction, and does not lose bromine when treated with acids or with dilute alkalis. In the air, and especially in sunlight, it becomes yellow. R. V. S.

Some Derivatives of Alloxan. GUIDO PELLIZZARI and C. CANTONI (*Gazzetta*, 1911, 41, i, 21—29. Compare Abstr., 1887, 1100; 1889, 519).—Alloxanphenylhydrazone can be obtained directly from alloxan by the use of phenylhydrazine hydrogen sulphite. The preparation is effected by saturating with sulphur dioxide an aqueous solution of alloxan in which phenylhydrazine is suspended.

Hydrazine hydrogen sulphite, under similar conditions, yields, in the cold, *alloxan bisulphite*, which forms colourless crystals. When it is boiled with water a reddish-yellow *substance* is formed, which is also obtained in addition to alloxantin when alloxan reacts with hydrazine hydrate at the ordinary temperature. The slight solubility of the substance, its acid character, and the fact that it does not react

with benzaldehyde accord with the formula (I),

$$\text{(I.)}\quad CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C:N\cdot NH_2$$

$$\text{(II.)}\quad CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C:N\cdot N:C<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO,$$

but the analytical figures agree with formula (II), which is, therefore, preferred by the authors.

Efforts have also been made to obtain substances of aldehydic nature by the action of alkalis or acids on phenylmethylpyrazolonealloxan in a manner similar to that which has been described in the case of other alloxan derivatives (compare Böhringer and Söhne, D.R.-P. 108026 [1898], 112174 [1899]). In no case was an aldehyde produced, and the formation of carbon monoxide or formic acid (which would accompany it) was not observed. When phenylmethylpyrazolonealloxan is boiled with hydrochloric acid (D 1·12, diluted with an equal volume of water), phenylmethylpyrazolonemalonylcarbamide (Abstr., 1889, 517) is first formed. This decomposes when the ebullition is continued, and a *hydrochloride* is obtained, of which the free *base* has m. p. 175—180°; phenylhydrazine oxalate and phenylmethylpyrazolone are also produced. R. V. S.

Action of Cyanogen Halides on Phenylhydrazine. III. GUIDO PELLIZZARI (*Gazzetta*, 1911, **41**, i, 54—59. Compare Abstr., 1892, 1323; 1907, i, 873).—Another substance can be isolated from the mother liquors of the products of the reaction between phenylhydrazine and cyanogen bromide in aqueous solution. It forms transparent crystals of a reddish tinge, which contain alcohol of crystallisation, and have m. p. 180°. The compound is identical with that described in the first paper, resulting from the polymerisation of β-cyanophenylhydrazide, but since it is stable towards alkali and acid, it has not the constitution there assigned to it, but is the corresponding cyclic compound, *diphenylaminoguanazole*,

$$NH:C<\begin{matrix}NPh\text{------}NH\\N(NHPh)\cdot C:NH\end{matrix}.$$

The *hydrochloride* and *picrate* have the properties formerly described.

α-Cyanophenylhydrazide reacts with cyanogen bromide in alcoholic solution at the ordinary temperature in the course of several days, forming *tricyanophenylhydrazide*, to which the constitution

$$CN\cdot NPh\cdot N(CN)_2$$

is provisionally given. It is a crystalline substance having a red or yellow tinge, and does not melt at 300°. The molecular weight in phenolic solution is normal. R. V. S.

Peculiar Reactions of the Diazo-compound of *p*-Aminobenzeneazosalicylic Acid. CARL BÜLOW [with KARL HAAS] (*Ber.*, 1911, **44**, 601—614).—Previously the author has observed that diazo-salts of certain substances containing the *p*-aminobenzeneazo-group yield intensely blue solutions by treatment with sufficient sodium carbonate or acetate. The source of this blue coloration has now been investigated in the case of the diazo-compound of *p*-aminobenzeneazosalicylic acid.

p-Acetylaminobenzeneazosalicylic acid,

$$NHAc\cdot C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H,$$

yellowish-brown prisms, m. p. 235°, obtained by coupling diazotised acetyl-*p*-phenylenediamine and salicylic acid in a solution containing sodium carbonate and hydroxide and acidifying the product, is hydrolysed best by concentrated sulphuric acid on the water-bath; the solution yields, after dilution with water, a *sulphate*, $(C_{13}H_{11}O_3N_3)_2,H_2SO_4$, from which sodium carbonate produces a sodium salt, which is decomposed by acetic acid, yielding p-*amino-benzeneazosalicylic acid*, a dirty, greyish-green powder, decomp. 232°. The aminoazo-compound is dissolved in dilute potassium hydroxide, treated with hydrochloric acid, and finally with sodium nitrite at 20—25°, whereby the *chloride* of the diazotised *p*-aminobenzene-azosalicylic acid is obtained in small, brick-red needles. By stirring a suspension of the chloride in cold water for four hours, a black *anhydride*, exploding at 132°, is obtained, to which the constitution $\begin{array}{l} N\cdot C_6H_4\cdot N{:}N\cdot O \\ \|\qquad\qquad\qquad\quad | \\ N\cdot C_6H_3(OH)\cdot CO \end{array}$ is ascribed.

When the diazo-chloride is added to an excess of aqueous sodium carbonate (not hydrogen carbonate, acetate, or hydroxide) at 0°, an intense blue solution is obtained, the colour of which persists for more than two hours and then becomes brown. By passing carbon dioxide into the blue solution, the colour changes to yellow; both solutions couple with *R*-salt. When the diazo-chloride is dissolved in dilute sodium hydroxide at 0° a blue solution is not obtained, but by passing in carbon dioxide the solution becomes blue, and finally yellow. These colour changes are explained by ascribing the blue coloration to the formation of the normal diazotate,

$$ONa\cdot N{:}N\cdot C_6H_4\cdot N{:}N\cdot C_6H_3(OH)\cdot CO_2Na,$$

and the yellow to the hydroxy-compound,

$$OH\cdot N{:}N\cdot C_6H_4\cdot N{:}N\cdot C_6H_3(OH)\cdot CO_2Na;$$

in sodium hydroxide the normal diazotate adds on NaOH to form

$$ONa\cdot N(OH)\cdot NNa\cdot C_6H_4\cdot N{:}N\cdot C_6H_3(ONa)\cdot CO_2Na,$$

which is converted by carbon dioxide successively into the blue and the yellow compounds.

*Ethyl acetoacetate-azobenzene-*p*-azosalicyclic acid*,

$$CO_2Et\cdot CHAc\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H,$$

m. p. 236° (decomp.), yellowish-brown needles, obtained by condensing the diazo-chloride of *p*-aminobenzeneazosalicylic acid with ethyl aceto-acetate in dilute alcohol in the presence of sodium acetate, has been converted into the following substances. With 60% hydrazine hydrate in glacial acetic acid, it yields 5-*hydroxy*-3-*methylpyrazole*-4-*azobenzene*-4′-p-*azosalicylic acid*,

$$\left.\begin{array}{l} N{=\!=\!=}CMe \\ | \\ NH\cdot C(OH) \end{array}\right\rangle C\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H,$$

m. p. above 300°. With phenylhydrazine in hot glacial acetic acid it yields 5-*hydroxy*-1-*phenyl*-3-*methylpyrazole*-4-*azobenzene*-4′-p-*azo-salicylic acid*, $C_{23}H_{18}O_4N_6$, m. p. 272—273° (decomp.). With 2:4-dinitro-phenylhydrazine, it yields a *dinitrophenylhydrazone*, $C_{25}H_{22}O_9N_8$, m. p. 252—253° (decomp.), which is converted by hot acetic anhydride

into 5-*hydroxy*-1-o : p-*dinitrophenyl*-3-*methylpyrazole*-4-*azobenzene*-4′-p-*azosalicylic acid*, $C_{23}H_{16}O_8N_8$, m. p. 202—203°. With hydroxylamine in diluted acetic acid it yields 5-*hydroxy*-3-*methyl*iso*oxazole*-4-*azobenzene*-4′-p-*azosalicylic acid*, m. p. 243—244°. By prolonged boiling with semicarbazide in diluted acetic acid, it yields 5-*hydroxy*-1-*carbamido*-3-*methylpyrazole*-4-*azobenzene*-4′-p-*azosalicylic acid*,

$$C_{18}H_{15}O_5N_7,$$

m. p. above 280°. The colour reactions of these substances with various reagents are described. C. S.

Some Derivatives of *p*-Aminobenzhydrol. HENRY A. TORREY and C. W. PORTER (*J. Amer. Chem. Soc.*, 1911, 33, 56—59).—The work described in this paper was carried out as part of an extensive investigation of the derivatives of *p*-aminobenzophenone.

Benzhydrol-4-azo-β-naphthol, $OH\cdot CHPh\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH$, m. p. 169·5°, is a bright red dye, which is precipitated when a solution of β-naphthol in sodium hydroxide is added to the diazotisation product of *p*-aminobenzhydrol. The *compound*, $C_6H_5\cdot CO\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH$, m. p. 185—186·5°, obtained in a similar manner from *p*-aminobenzophenone, is a dye of a much lighter red colour, and forms feathery crystals.

Benzhydrol-4-azodimethylaniline, $OH\cdot CHPh\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NMe_2$, m. p. 145°, is a dye, which forms red, lustrous flakes; its *acetyl* and *benzoyl* derivatives were prepared.

Salicylidene-p-*aminobenzhydrol*, $OH\cdot CHPh\cdot C_6H_4\cdot N{:}CH\cdot C_6H_4\cdot OH$, m. p. 76—79°, obtained by heating a solution of *p*-aminobenzhydrol and salicylaldehyde in alcohol, forms yellow crystals. *Salicylidene*-p-*aminobenzophenone*, $C_6H_5\cdot CO\cdot C_6H_4\cdot N{:}CH\cdot C_6H_4\cdot OH$, is a yellow, crystalline solid, which is insoluble in solution of sodium hydroxide.

β-Naphtholaldehyde condenses with *p*-aminobenzhydrol to form the *compound*, $OH\cdot CHPh\cdot C_6H_4\cdot N{:}CH\cdot C_{10}H_6\cdot OH$, m. p. 167·5°, which is obtained in yellow crystals. The corresponding *compound*,

$$C_6H_5\cdot CO\cdot C_6H_4\cdot N{:}CH\cdot C_{10}H_6\cdot OH,$$

m. p. 152°, obtained from *p*-aminobenzophenone, also forms yellow crystals. E. G.

The Stability towards Light of Methylated Hydroxyazo-dyes. Some Derivatives of 1-Methoxynaphthalene. N. N. VOROSCHCOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 1458—1465).—The introduction of an alkyl group into the hydroxy-group of a hydroxyazo-dye might be expected to result in an increase of the stability towards light, since the hydroxy-group is the most highly reactive of the molecule, and since replacement of its hydrogen by a metal is, in general, accompanied by increase of this stability.

Examination of the methoxy-derivatives corresponding with a number of hydroxyazonaphthalenesulphonic acids, prepared by Colombano's method (Abstr., 1907, i, 1091), shows, however, that the stability of these colouring matters towards light is not increased by the replacement of the hydroxy- by methoxy-groups.

Reduction of 1-sulphonaphthalene-4-azoanisole by means of zinc and acetic acid yields *p*-anisidine, which was identified through its acetyl

derivative. In a similar manner, colouring matters containing the 1-methoxynaphthalene group may be converted into 4-*acetylamino*-1-*methoxynaphthalene*, $OMe\cdot C_{10}H_6\cdot NHAc$, which forms colourless prisms, m. p. 180—181°, and may also be prepared by reducing 4-nitro-1-methoxynaphthalene and subsequently acetylating.

Sodium 1-*methoxynaphthalene*-4-*sulphonate*, $OMe\cdot C_{10}H_6\cdot SO_3Na$, prepared by treating α-naphthol-4-sulphonic acid with methyl sulphate and sodium hydroxide, forms shining plates containing $3H_2O$, and the corresponding barium salt forms nacreous crystals.

4-*Nitro*-1-*methoxynaphthalene*, $OMe\cdot C_{10}H_6\cdot NO_2$, obtained by adding a mixture of sodium 1-methoxynaphthalene-4-sulphonate and sodium hydrogen carbonate to a solution of carbamide in nitric acid, forms yellow needles, m. p. 81°. T. H. P.

Azo-derivatives of 3-Phenyl*iso*oxazolone. André Meyer (*Compt. rend.*, 1911, **152**, 610—612. Compare Abstr., 1910, i, 593). —The following derivatives of Claisen's 4-benzeneazo-3-phenyl*iso*oxazolone (Abstr., 1891, 468) were prepared by dissolving phenyl*iso*oxazolone in aqueous alkali and sodium acetate, and adding the calculated amount of a diazonium salt. The required compound was obtained in theoretical yield by precipitation with acetic acid. All the substances described melt with decomposition.

4-m-*Nitrobenzeneazo*-3-*phenyl*iso*oxazolone*, $C_{15}H_{10}O_4N_4$, bright yellow needles, m. p. 200—201°; the p-*nitro*-compound crystallises in orange needles, m, p. 224—225°.

4-o-*Tolueneazo*-3-*phenyl*iso*oxazolone*, $C_{16}H_{13}O_2N_3$, orange needles, m. p. 151—152°; the p-*toluene* derivative has m. p. 177—178°. The m-*nitro*-p-*toluene* compound has m. p. 205—206°; the o-*nitro*-p-*toluene* compound forms deep orange needles, m. p. 213—214°. 4-m-*Xyleneazo*-3-*phenyl*iso*oxazolone*, $C_{17}H_{15}O_2N_3$, orange needles, m. p. 187°. 4-ψ-*Cumeneazo*-3-*phenyl*iso*oxazolone*, bright red needles, m. p. 215—216°. 4-α-*Naphthaleneazo*-3-*phenyl*iso*oxazolone*, $C_{19}H_{13}O_2N_3$, slender, brown needles, m. p. 172—173°; the β-derivative forms deep yellow needles, m. p. 202—203°. 4-o-*Carboxybenzeneazo*-3-*phenyl*iso*oxazolone*,

$$C_{16}H_{11}O_4N_3,$$

bright yellow needles, m. p. about 245°; the m-*carboxy-acid* has m. p. about 260°, and the p-*carboxyl acid*, m. p. about 290°. *Phenyldimethylpyrazoloneazophenyl*iso*oxazolone*, $C_{20}H_{17}O_3N_5$, ruby-red needles, m. p. 196—197°. *Diphenylbisazobisphenyl*iso*oxazolone*, $C_{30}H_{20}O_4N_6$, is a brick-red powder, m. p. above 300°. W. O. W.

The Refractive Indices of Certain Proteins. III. Serum Globulin. IV. Casein in Alcohol-Water Mixtures. T. Brailsford Robertson (*J. Biol. Chem.*, 1910, **8**, 441—448, 507—511. Compare Abstr., 1910, i, 526, 793).—The value of a for serum globulin under different conditions varies from 0·00229 to 0·00119, and for casein from 0·00157 to 0·00125. W. D. H.

Hydrolysis of the Protein of Linseed. F. W. Foreman (*J. Agric. Science*, 1911, **3**, 358—382; *Proc. Camb. Phil. Soc.*, 1911, **16**, 87—88).—The protein of linseed meal, extracted with 0·2% potassium

hydroxide, contains 17·45% nitrogen. When hydrolysed with hydrochloric acid (D 1·16), the following substances were obtained: alanine, 1·03; valine, 12·71; leucine and *iso*leucine, 3·97; proline, 2·85; phenylalanine, 4·14; aspartic acid, 1·65; glutamic acid, 11·58; tyrosine, 0·65; arginine, 6·06; histidine, 1·66; lysine, 1·19; and ammonia, 1·94%. Small amounts of glycine, serine, and tryptophan were also found.

The most striking result is the high amount of valine; the highest percentage hitherto obtained by the hydrolysis of proteins seems to be only 2%. N. H. J. M.

Thymic Acid. HERMANN STEUDEL and P. BRIGL (*Zeitsch. physiol. Chem.*, 1910, 70, 398—403).—By the action of dilute nitric acid in the cold on thymus-nucleic acid, the alloxuric bases are eliminated and a compound, $C_{33}H_{51}O_{31}N_5P_4$, remains, for which the name *thymic acid* is suggested. This contains all the phosphoric acid of nucleic acid in an organic complex, is dextrorotatory, and forms a barium salt. It does not reduce Fehling's solution after purification. When hydrolysed, it yields thymin and uracil in the proportions required by the formula given. E. F. A.

The Action of Dilute Acids and Salt Solutions on Gelatin. HENRY R. PROCTER (*Koll. Chem. Beihefte*, 1911, 2, 243—284).—The action of solutions on the connective tissue is complicated by their capillary absorption between the fibres of collagen, of which it mainly consists. To avoid this difficulty, the author has studied the action of solutions or thin sheets of gelatin, which is a chemically closely related substance. In opposition to the view that gelatin jelly has ordinarily the microscopic cellular structure attributed to it by Bütschli and van Bemmelen, normal jelly is considered to be a network of protein molecules, in which the absorbed liquid is dissolved and subjected to its molecular attractions and internal pressure. The swelling of gelatin is thus an osmotic phenomenon, which, however, is influenced not only by the presence of altered products formed by hydrolysis, but also by the solid elasticity dependent on its volume at the moment of solidification.

Gelatin jelly is insoluble in alcohol, and semipermeable to it, and its dehydration is due to the external osmotic pressure of the alcohol. If, however, alcohol is incorporated with gelatin solution before "setting," it forms a mixture, which, although apparently homogeneous, must really be an emulsion of diluted alcohol. Such a jelly swells in water more than a purely aqueous one, since the alcohol globules become diluted in equilibrium with the jelly. Such jellies would probably show microscopic cellular structure.

Swelling with acids is a more complex phenomenon, and apparently involves chemical combination as well as osmotic action. Gelatin, which absorbs only seven or eight times its weight of pure water, may absorb over fifty times its weight of 0·005*N*-hydrochloric acid solution, but it contracts again when the acid solution is concentrated, absorbing only twenty times its weight of 0·2*N*-acid. In more concentrated solutions the jelly dissolves.

The amount of acid in the jelly increases with that in the outer solution, and is always in excess of that corresponding with the solution absorbed. Since only a portion of the absorbed acid can be estimated by titration with methyl-orange as indicator, it is evident that part of the acid is in some way combined. Assuming that the concentration of the free acid in the absorbed solution is the same as that in the outer solution, and deducting this from the total acid in the jelly, it is found that the acid "fixed" by 1 gram of dry gelatin increases rapidly up to a concentration of about $0{\cdot}005N$-acid, and afterwards remains nearly constant. This constant value corresponds with about 0·78 mg. mol. of acid per gram of gelatin.

In hydrochloric acid solutions of greater concentration than $0{\cdot}005N$, the swelling is repressed by increasing the concentration of the chlorine ion. By addition of sodium chloride, this repression can be carried almost to dehydration, although neutral gelatin is swollen by salt solutions. The total acid in the contracted jelly is diminished by that expelled, but the "fixed" acid is increased, and sodium chloride is expelled from the solution absorbed. The effect is evidently due to osmotic forces, although, since both hydrogen and sodium chlorides and their ions diffuse freely through gelatin, the condition of equilibrium would appear to resemble that which is set up in the distribution of a substance between immiscible solvents.

It is assumed that the amphoteric gelatin forms a hydrolysable chloride in equilibrium with the acid having a much greater affinity for water than for neutral gelatin. If x is the molar concentration of the external acid, β the number of millimols. in the jelly per gram of gelatin, and k the hydrolytic constant, then $\beta = x/x + k$ is the proportion of unhydrolysed salt. Taking β as 1·28 and k as 0·005, a curve representing the values of fixed acid is obtained, which corresponds closely with the experimental curve when the swelling is repressed by large quantities of sodium chloride, although it is higher than the experimental curve in the absence of salt. The assumption that the free acid in the absorbed solution is of the same concentration as the outer solution is, however, not strictly permissible, for the chlorine ion concentration in the ionised gelatin chloride must be equal to that of the outer solution, and since the gelatin ion cannot diffuse, this equality can only result from the expulsion of water and acid.

The experimental curve of swelling can be represented by the expression $7{\cdot}8\sqrt{x/x+k}$, and the curve of total acid absorbed by $(7{\cdot}8x^{\frac{3}{2}}/x+k)+0{\cdot}8$, or by the adsorption formula $\eta = 87x^{0{\cdot}41}$. If the hydrolytic constant k be taken as 0·005, the ionisation constant of neutral gelatin is of the order of 1×10^{-12}.

Similar considerations to the above are applicable to the equilibrium between gelatin and solutions of weak acids and their salts, data for which are also recorded in the paper. H. M. D.

Trypsin and Pancreas Nucleo-protein. Leonor Michaelis and Heinrich Davidsohn (*Biochem. Zeitsch.*, 1911, **30**, 481—504).—The isoelectric point of trypsin was determined by two methods, namely, by dissolving the trypsin in solutions with different hydrogen ion concentrations and determining the range of concentration in

which it is neither distinctly anodic or cathodic when in an electric field (method of electrocataphoresis), and by determining the hydrogen ion concentration in which aggregation most readily takes place. In the former experiment a silver anode in concentrated sodium chloride, and, as cathode, copper wire and a moderately concentrated cupric chloride solution were employed. By the first of the above-mentioned methods, the isoelectric point was found to be about $H = 1{\cdot}35 \times 10^{-4}$, and by the second, $2{\cdot}6 \times 10^{-4}$. This is almost the same as the isoelectric point found for Hammarsten's α-nucleo-protein, and differs considerably from that of the β-nucleo-protein ($H = 1{\cdot}2 \times 10^{-3}$), and of the protein which can be obtained from this ($H = 1{\cdot}7 \times 10^{-5}$). Furthermore, no organ other than the pancreas yields a substance of the same isoelectric point. If trypsin be aggregated from its solution under the optimal conditions, a strong trypsin preparation is obtained, as the greater part of the enzyme is carried down in the precipitate, which does not give the normal protein reactions. From the results, the authors conclude that there is probably an intimate chemical relationship between trypsin and α-nucleo-protein. S. B. S.

Optically Active Compounds of Phosphorus. JAKOB MEISENHEIMER and LEO LICHTENSTADT (*Ber.*, 1911, **44**, 356—359. Compare Abstr., 1909, i, 20).—It has been shown previously that the bases obtained from *d*- and *l*-hydroxyphenylmethylethylammonium chlorides, OH·NMeEtPhCl, by the action of barium hydroxide are optically active, but it was left uncertain whether they had the formula O:NMeEtPh or $NMeEtPh(OH)_2$. The conclusion is now arrived at that the crystalline solid is an amine oxide, but that in aqueous solution the dihydroxy-form is present. A cyclic amine oxide, kairoline oxide, has been observed to behave similarly, and the same process has been investigated with phosphine oxides.

Phenylmethylethylphosphine oxide, O:PMeEtPh, prepared by the addition of methyl iodide to ethyldiphenylphosphine and subsequent boiling with water, is a colourless, hygroscopic substance crystallising in needles, m. p. about 50°, b. p. above 360° without decomposition. With *d*-bromocamphorsulphonic acid a well crystallised salt is formed, having m. p. 94—95° and $[\alpha]_D + 67{\cdot}4°$, which values did not change on fractional crystallisation. The value for the rotation indicates the presence of an optically-active phosphorus ion.

d-*Methylethylphenylphosphine oxide* is obtained by the action of ammonia on the salt in benzene solution in crystalline needles, $[\alpha]_D + 23{\cdot}1°$ in water, and 33·8° in benzene.

Accordingly, the free phosphine oxide is optically active, and the satisfaction of the five valencies of phosphorus with only four different radicles is sufficient to give asymmetric compounds. E. F. A.

Organic Chemistry.

$\beta\gamma$-Dimethylhexane. LATHAM CLARKE (*J. Amer. Chem. Soc.*, 1911, **33**, 520—531).—In continuation of the work on the octanes (Abstr., 1907, i, 169; 1908, i, 493, 593; 1909, i, 125, 350), $\beta\gamma$-dimethylhexane has been synthesised by the two following methods: (1) Ethyl dimethylacetoacetate on hydrolysis yields dimethylacetone (β-methyl-γ-butanone), which on treatment with magnesium propyl bromide gives $\beta\gamma$-dimethyl-γ-hexanol. This compound is converted into γ-iodo-$\beta\gamma$-dimethylhexane by the action of iodine in presence of amorphous phosphorus, and on reducing this substance with zinc and hydrochloric acid, $\beta\gamma$-dimethylhexane is produced. (2) Ethyl methylpropylacetoacetate on hydrolysis yields γ-methyl-β-hexanone, which on treatment with magnesium methyl iodide is converted into $\beta\gamma$-dimethyl-β-hexanol. From the latter compound, β-iodo-$\beta\gamma$-dimethylhexane is prepared, which on reduction gives $\beta\gamma$-dimethylhexane.

$\beta\gamma$-Dimethyl-γ-hexanol, $CHMe_2\cdot CMe(OH)\cdot CH_2\cdot CH_2Me$, b. p. 158—158·2°/758 mm., has a eucalyptus-like odour: *$\beta\gamma$-Dimethylhexane*, $CHMe_2\cdot CHMe\cdot CH_2\cdot CH_2Me$, b. p. 113·8—114°/758 mm., is a colourless, mobile liquid, which has a rather strong odour, D_{15}^{15} 0·7246, and n_D^{25} 1·4075.

γ-Methyl-β-hexanone has b. p. 136—137°/760 mm. *$\beta\gamma$-Dimethyl-β-hexanol*, $OH\cdot CMe_2\cdot CHMe\cdot CH_2\cdot CH_2Me$, b. p. 150—151°/756 mm., is a colourless liquid with an odour recalling that of musty apples.

The physical constants of eight octanes are compared, and it is shown that these compounds fall into three classes according to the number of methyl groups they contain, *n*-octane containing two, the methylheptanes three, and the dimethylhexanes four methyl groups. The volatility increases with the number of methyl groups present. The position of the methyl group in the methylheptanes makes only a slight difference in the boiling point, but the density increases as the methyl group is moved successively from the β- to the γ- or δ-position.

E. G.

Pyrogenic Decomposition of *s*-Tetrachloroethane and Trichloroethylene. O. NICODEMUS (*J. pr. Chem.*, 1911, [ii], **83**, 312—322).—The liquid under examination is heated nearly to the boiling point in a flask through which a current of purified carbon dioxide is drawn; the gas and vapour pass into a quartz combustion tube packed with pumice and heated electrically by about six metres of nickel wire (1 mm. thick, resistance 2·2 ohms) wound round the tube and insulated by asbestos cord, loss of heat being diminished by wrapping the tube and wire in layers of asbestos paper. The current is supplied at 72 volts; the temperature desired is attained after one and a-half to two hours, and is determined by a platinum-iridium thermocouple. The quartz tube is connected with a series of condensing vessels consisting of a large Woulf's bottle, two washing-bottles

containing ether (in ice), two containing water, and the gasometer. The gas and vapour pass through the tube at such a rate that the deposition of carbon in the tube is as small as possible, and the vapour streaming into the Woulf's bottle has a light brown colour. The products obtained by the decomposition of *s*-tetrachloroethane at 700° under these conditions cannot be separated satisfactorily by fractional distillation; consequently, the author collects fractions at every 10°, and treats each with bromine in sunlight, whereby the saturated chlorinated components are unattacked, whilst the unsaturated constituents are converted into chlorobromo-derivatives of high boiling point, the separation of which is readily effected by fractional distillation. In this way the author has obtained *s*-dichloroethylene, 1—5%; chloroform, 5—8%; carbon tetrachloride, 5—8%; trichloroethylene, 50—60%; tetrachloroethylene, 5—10%; pentachloroethane, 1—3%; and hexachloroethane, 1—3%, the percentages being calculated on the amount of crude decomposition products; the remainder consists of carbon and hexachlorobenzene.

Under conditions similar to the preceding, trichloroethylene decomposes violently, and yields dichloromethane (a trace); dichloroethylene, 5—10%; chloroform, 5—10%; tetrachloroethylene, 5—10%; carbon tetrachloride, 5—10%; $\alpha\beta\beta\beta$-tetrachloroethane, 3—5%; pentachloroethane, 3—5%; and hexachloroethane (a trace). When the decomposition is performed slowly a large quantity of carbon and hexachlorobenzene is produced; by rapid distillation, free chlorine is formed together with dichloroacetylene (?), which partly polymerises and partly explodes in the delivery tube. The fraction, b. p. 180—230°, contains about 15% of *$\alpha\alpha\alpha\gamma\delta\delta$-hexachloro-$\Delta^{\beta}$-butylene*,

$$CCl_3{\cdot}CH{:}CCl{\cdot}CHCl_2\ (?),$$

b. p. 210—212° (decomp.) or 98—99°/17 mm., D_{30}^{30} 1·6610, the constitution of which is deduced from the facts that quinoline eliminates hydrogen chloride (1 mol.), yielding a *substance*, C_4HCl_5, b. p. 227—230° or 130°/80 mm., sodium ethoxide produces an *ether*, $C_3HCl_3(OEt)_3$, b. p. 240—245°/120 mm., and reduction by zinc and acetic acid gives products from which allyl chloride and trichloropropylene have been isolated. The fraction, b. p. 240—300°, contains pentachlorobenzene, m. p. 85—86° (identified by conversion into pentachloronitrobenzene by nitration), and 2 : 3 : 4-*trichlorobenzylidene chloride*, $C_6H_2Cl_3{\cdot}CHCl_2$, m. p. 83—84°, b. p. 275—280°, which is converted by hydrochloric acid into the trichlorobenzaldehyde, m. p. 91°. The fraction, b. p. 300—340°, representing 20—25% of the crude products of decomposition, consists almost entirely of hexachlorobenzene, but also contains about 0·3—0·5% of 2 : 3 : 5 : 6-*tetrachlorobenzotrichloride*, $C_6HCl_4{\cdot}CCl_3$, m. p. 101—102°, b. p. 320—330°, which is not attacked by chlorine, bromine, or potassium permanganate, but is oxidised by chromic acid to chloranil, and is converted by alcoholic potassium hydroxide into the *ester*, $C_6HCl_4{\cdot}C(OEt)_3$, b. p. 240—245°/120 mm. C. S.

Tribromo*tert*.-butyl Alcohol, $C_4H_7OBr_3$. THOMAS B. ALDRICH (*J. Amer. Chem. Soc.*, 1911, 33, 386—388).—Willgerodt (Abstr., 1882, 492) has described the preparation of chloro*tert*.-butyl alcohol

(chloretone) by the action of alkali hydroxide on a mixture of chloroform and acetone. An account is now given of the corresponding tribromo-derivative (brometone), the pharmacological action of which has been studied by Houghton and Aldrich (Abstr., 1903 ii, 315).

Tribromo*tert.*-butyl alcohol, $CBr_3\cdot CMe_2\cdot OH$, m. p. 167—176°, forms white crystals, has a camphor-like taste and odour, is slowly volatile in the air, and can be distilled with steam. This compound, like the trichloro-derivative, contains varying amounts of water, which are present in the form of a solid solution (compare Cameron and Holly, Abstr., 1899, i, 323). Attempts have been made to convert tribromo-*tert.*-butyl alcohol into α-hydroxy*iso*butyric acid, which was obtained by Willgerodt (*loc. cit.*) from the trichloro-derivative, but, although an organic acid was produced, the quantity was too small for it to be identified. E. G.

Method for Preparing Certain True Acetylenic Alcohols. ROBERT LESPIEAU (*Compt. rend.*, 1911, **152**, 879—881).—The next higher homologue of butinene-γ-ol has been prepared by the method previously described, which appears to be of general application (Abstr., 1910, i, 149).

Δ^{α}-Pentinene-γ-ol, $OH\cdot CHEt\cdot C\vdots CH$, b. p. 125°/761 mm., has D^{15} 0·8926, n_D 1·4347. It forms a crystalline precipitate with aqueous silver nitrate, soluble in excess, having the composition

$$C_5H_7OAg,AgNO_3.$$

The precipitate formed with cuprous chloride is soluble in ammonia; on treatment with iodine it yields *$\alpha\alpha\beta$-tri-iodo-Δ^{α}-penten-γ-ol*,

$$OH\cdot CHEt\cdot CI\colon CI_2,$$

m. p. 142—144°. *β-Bromo-Δ^{α}-penten-γ-ol*, $OH\cdot CHEt\cdot CBr\colon CH_2$, has b. p. 165—166°/755 mm., $D^{15\cdot5}$ 1·351, n_D 1·482; the *phenylurethane* has m. p. 42—44°.

Acetylenic alcohols can also be obtained, although not in good yield, by the action of acraldehyde on zinc alkyl derivatives or organomagnesium halides.

$\alpha\beta$-Dibromopentan-γ-ol, heated with sodium ethoxide, gave the *oxide*, $O<\begin{matrix}CH\cdot CH_2Br\\ |\\ CHEt\end{matrix}$, b. p. 165—166°/768 mm., $D^{15\cdot5}$ 1·4096, n_D 1·4725.

W. O. W.

Quantitative Dehydration of Pure Pinacone. MAURICE DELACRE (*Bull. Soc. chim.*, 1911, [iv], **9**, 240—247).—Couturier has pointed out that quantitative yields of pinacolin should be obtained by the dehydration of pinacone (Abstr., 1893, i, 244), and this conclusion has been confirmed by Richard and Langlais (Abstr., 1910, i, 455). In the present paper details are given of the yields obtained by the use of sulphuric and oxalic acids as dehydrating agents, and it is shown that high yields are obtainable when pure pinacone is employed, and if this condition is fulfilled Friedel's process gives results as good as those obtained by methods suggested more recently. T. A. H.

Pyrogenic Decomposition of Metallic Xanthates. ALEXANDRE HÉBERT (*Compt. rend.*, 1911, **152**, 869—871. Compare Fleicher and Hankó, Abstr., 1878, 29).—A tabular statement shows the relative proportions of the principal products obtained by decomposing at 350° the xanthates of potassium, barium, iron, cobalt, nickel, zinc, copper, lead, mercury, silver, and tin. The gases liberated consist of hydrogen sulphide and carbon dioxide, with small quantities of combustible gases containing carbon monoxide.

The liquid products as a rule contain carbon disulphide, carbon oxysulphide, ethyl alcohol, ethyl hydrogen sulphide, and ethyl sulphide and disulphide. In the case of the nickel and silver salts, however, the liquid is composed almost entirely of ethyl xanthate, and the dry distillation of the nickel salt is recommended as a useful method for preparing this substance. W. O. W.

Catalytic Scission of Esters by Certain Metallic Oxides. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1911, **152**, 669—673. Compare Senderens, Abstr., 1908, i, 494, 495; 1909, i, 127, 286; Colson, Abstr., 1909, i, 302).—If the catalyst is heated above 330° during the esterification of acids by the method previously described (this vol., i, 258), the yield of ester is diminished; at 400°, the principal reactions are those involving decomposition of the acid and alcohol.

When the vapour of an ester is passed over the catalyst, decomposition may occur in several ways. In each case it is supposed that an unstable salt and alkyloxide are first formed, and that the course of the subsequent reactions depends on the relative stability of these substances. They are produced in accordance with the equation: $2MO + 2R\cdot CO_2\cdot C_nH_{2n+1} = (R\cdot CO_2)_2M + (C_nH_{2n+1}O)_2M$. (1) If the salts are equally unstable, a ketone and ethylenic hydrocarbon (2 vols.) with carbon dioxide (1 vol.) and water are formed, for example, when ethyl acetate is passed over alumina. (2) When the alkyl oxide is more stable the water formed in (1) reacts with it, giving an alcohol. Thus ethyl, propyl, and *iso*butyl acetates, propyl propionate, and ethyl hexoate, in presence of thorium oxide, yield a ketone and alcohol with approximately equal volumes of hydrocarbon and carbon dioxide. At high temperatures, however, the alcohol undergoes dehydrogenation. (3) When the converse holds, as, for example, when titanium oxide is the catalyst, the salt $(R\cdot CO_2)_2M$, is decomposed by water, yielding the acid. (4) If the ester is a benzoate or toluate, or if boric anhydride is used as catalyst, exclusive formation of acid and unsaturated hydrocarbon occurs. Thus ethyl valerate is decomposed by boric anhydride at 400° into ethylene and valeric acid. W. O. W.

Density of Soap Solutions. E. C. V. CORNISH (*Zeitsch. physikal. Chem.*, 1911, **76**, 210—211).—The measurements were made by the pyknometer method at 90°. Some of the results are as follows: Sodium palmitate, $N/1$ $D_4^{90} = 0{\cdot}9625$, $N/2$ 0·9658, $N/10$ 0·9654, $N/100$ 0·9655; sodium stearate, $N/2$ 0·9599, $N/10$ 0·9629, $N/100$ 0·9639. D_4^{90} for water is 0·9653. G. S.

Constitution of Soap Solutions: Solutions of "Sodium Palmitates." JAMES W. MCBAIN and MILLICENT TAYLOR (*Zeitsch. physikal. Chem.*, 1911, **76**, 179—209. Compare Abstr., 1910, ii, 177).—The high electrical conductivity of aqueous solutions of sodium palmitate at 90° (*loc. cit.*) shows that the normal soaps are not simple colloids. The nature of the dissolved electrolyte is not conclusively established; it is certain that free sodium hydroxide is present, and presumably normal sodium palmitate is present in ordinary solution, and acid sodium palmitate mainly in the colloidal form. As the conductivity does not alter with time, there is a completely reversible equilibrium between electrolyte, hydrosol, and coagulum. The molecular conductivity-dilution curve of sodium palmitate is unlike any previously observed in aqueous solution, inasmuch as it shows a pronounced maximum in half-normal and a distinct minimum between $N/5$- and $N/10$-solution. The conductivity of solutions containing sodium hydroxide and sodium palmitate in varying proportions has also been investigated; the results show that even in normal solution sodium palmitate is considerably hydrolysed.

The solubility of palmitic acid and of acid sodium palmitate in water has been investigated. If it is assumed that the palmitic acid is dissociated to the extent of 50% in aqueous solution, the concentration of the undissociated acid, and also of the ions, is about $0{\cdot}6 \times 10^{-5}$ mol. per litre at 90°. The conductivity of a saturated solution of acid sodium palmitate is due mainly to ionised normal and acid palmitate, and to a much smaller extent to the presence of sodium hydroxide.

The precipitate obtained by "salting out" sodium palmitate with sodium hydroxide consists mainly of sodium acid palmitate with proportions of the normal palmitate depending upon the conditions of precipitation.

The boiling point and vapour-pressure methods are inapplicable to the investigation of soap solution, owing to the great difficulty of removing adsorbed air. G. S.

Direct Synthesis of the Glycerides. G. GIANOLI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 348).—The author points out that the method described by Bellucci and Manzetti in a recent paper under this title (this vol., i, 259) is not new, for it was introduced by him on the large scale in 1891, and was referred to in a recent publication (Gianoli, *Atti VI. Congr. chim. appl.*, 1907, **3**, 51). R. V. S.

Mode of Formation of Ethyl Chloroethoxyacetate. Use of this Ester in the Synthesis of α-Alkyloxy-acids. EDMOND É. BLAISE and L. PICARD (*Compt. rend.*, 1911, **152**, 960—962).—In an attempt to prepare diethoxyacetyl chloride by the action of thionyl chloride on diethoxyacetic acid, a liquid was obtained giving on fractionation an anhydride of glyoxylic acid, with the chloride, OEt·SOCl, and a liquid, b. p. 79—81°/10 mm. The latter has the composition of the expected chloride, but proved to be *ethyl chloroethoxyacetate*,

$$OEt{\cdot}CHCl{\cdot}CO_2Et.$$

This yields α-alkyloxy-esters on treatment with zinc alkyl halides; thus zinc propyl iodide furnishes ethyl α-ethoxyvalerate.

Ethyl chloroethoxyacetate is not formed in the chlorination of ethoxyacetic acid, but may be prepared by the action of thionyl chloride on the alcoholate of ethyl glyoxylate. The production of the ester from diethoxyacetic acid is probably preceded by the formation of the chloride, which then undergoes transformation, involving interchange of the chlorine atom with an ethoxy-group. W. O. W.

Keto-enolic Tautomerism. KURT H. MEYER (*Annalen*, 1911, **380**, 212—242).—I. *The Quantitative Estimation of Keto-enolic Tautomerides.*—It is shown, by experiments with compounds which exist in both the ketonic and enolic forms, that the unsaturated hydroxylic compound reacts instantaneously with an alcoholic solution of bromine, and that the amount of bromine used up corresponds with the formation of a dibromide. The ketonic forms, on the other hand, are coloured by the first drop of bromine solution, and the colour disappears gradually. The compounds experimented with were the two forms of dibenzoylacetylmethane, mesityl-oxide-oxalic ester and diacetylsuccinic ester, and the pairs of compounds, anthranol and anthrone, anthraquinol and hydroxyanthrone.

When other solvents are used, for example, benzene or chloroform, the difference between the ketonic and enolic forms is not so marked (compare also Lapworth, Trans., 1904, **85**, 30). The reaction between the enol and bromine undoubtedly consists in the formation of a dibromide (compare Lippmann, *Zeitsch. Chem.*, 1869, **5**, 29), although such products cannot be isolated, as hydrogen bromide is immediately liberated and a bromo-ketone is formed.

The amount of the enolic compound in a mixture of the tautomeric forms can also be determined by the aid of bromine. A simple method consists in titrating the alcoholic solution with an alcoholic solution of bromine of known concentration, until the colour of the bromine remains permanent. The method has the disadvantage that alcoholic solutions of bromine rapidly deteriorate. A more general method consists in titrating with an alcoholic solution of bromine of unknown concentration, and then determining the amount of bromo-ketone formed. This is accomplished by adding potassium iodide solution and warming gently, when iodine is liberated, owing to the reduction of the bromo-ketone to ketone. The iodine liberated is titrated by means of standard thiosulphate without the aid of starch. The reaction probably consists in the addition of hydrogen iodide to the carbonyl group, and the replacement of bromine by iodine and ultimately in the elimination of iodine from the di-iodo-compound : $O{:}\overset{|}{C}{\cdot}CBr{<} \longrightarrow OH{\cdot}\overset{|}{C}I{\cdot}CI{<} \longrightarrow$ $OH{\cdot}\overset{|}{C}{:}C{<} + I_2$.

When a $N/50$-solution of either the enolic or ketonic form of dibenzoylacetylmethane in alcohol is kept for twelve hours, an equilibrium mixture containing 75% of the enolic compound is obtained. In the case of the enolic form of methyl mesityl-oxide-oxalate, $CMe_2{:}CH{\cdot}CO{\cdot}CH{:}C(OH){\cdot}CO_2Me$, rather more than one molecule is used up before the red colour of the bromine persists for a moment

or two. This is probably due to the addition of bromine to the second ethylene linking. Benzoylacetone reacts with a carbon disulphide solution of bromine, yielding a *hydrobromide* of the ketone, which gives up hydrogen bromide on exposure to the air.

II. *Tautomerism of Ethyl Acetoacetate.*—Titrations of freshly-prepared solutions of ethyl acetoacetate indicate the presence of 7·71% of the enolic form. Similar results are obtained for the following solvents when the solutions are titrated immediately after they are prepared: methyl, ethyl, propyl and amyl alcohols, and chloroform at $-15°$, provided the titration is made in the presence of an excess of alcohol. These results indicate that the liquid ester contains 7·71% of enol and 92·29% of ketone (compare Hantzsch, Abstr., 1910, i, 811; Brühl, 1905, i, 407). Different results are obtained when the solutions are kept for some time. The following numbers indicate the percentage of enol present after forty-eight hours at 18°: Water 0·4, glacial acetic acid 5·74, methyl alcohol 6·87, acetone 7·3, chloroform 8·2, nitrobenzene 10·1, ethyl alcohol 12, ethyl acetate 12·9, benzene 16·2, ether 27·1, carbon disulphide 32·4, and hexane 46·4. In all cases an appreciable excess of ethyl alcohol was added before the titration with the bromine solution.

In solution a rise of temperature favours the formation of the ketonic form, for example, boiling methyl and ethyl alcoholic solutions contain respectively 4·74 and 7·5% of enol. Heating the liquid ester to 80° for an hour scarcely affects the equilibrium, but the freshly distilled ester contains 20—25% of enol.

When an alkaline solution of ethyl acetoacetate is acidified, an oil is precipitated which gradually dissolves. The oil is the enolic form, which is then transformed into the keto-form (99·6%), and these phenomena are in harmony with Dimroth's conclusion (this vol., ii, 31) that the relative proportions of the two components in a given solution when equilibrium is reached depend on the relative solubilities of the components. The enol, on the other hand, is readily soluble in hexane or light petroleum, and is removed when the liquid ester is shaken three times with twice its volume of well-cooled hexane; the residual oil after freeing from hexane contains only 1·5% of the enol.

The solubility of the keto-form in water at 0° is 11·6%, and in 2% sodium chloride solution 10·9%. The solubility of the enol in 2% sodium chloride solution is 0·5%. The value for the van 't Hoff-Dimroth constant G is thus 0·09.

The velocity of transformation has been calculated by means of the equations: $k_1 + k_2 = 1/(t_2 - t_1)\log s - x_1/s - x_2$ and $k_1/k_2 = C_2/C_1$. Where k_1 is the velocity constant of ketonisation, k_2 that of enolisation, s the value of x when equilibrium is attained, and C_1 and C_2 the concentrations of the two forms in the equilibrium mixture. For liquid ester which has been freshly distilled, the value for k_1 is 0·00055, and k_2 0·000046 at 15°.

In aqueous solution the values are $k_1 = 2·4$, and $k_2 = 0·010$ at 0°. The velocity of enolisation can also be determined by the rate of addition of bromine to the ketone, since this includes the enolisation of the ketone and the instantaneous addition of bromine to the enol (compare Lapworth, *loc. cit.*).

In 99·8% ethyl alcohol, $k_1 = 0·077$, and $k_2 = 0·0105$ at 0°; in hexane, $k_1 = 0·0041$, and $k_2 = 0·0035$ at 0°.

Acids have a catalytic action; thus, in aqueous 0·1*N*-hydrochloric acid at 0°, $k_2 = 0·018$; in non-ionising solvents the catalytic effect is much more marked. For example, when the ester is shaken for a few seconds with hexane containing a little hydrogen bromide, 45—46% of enol is found. It is suggested that the action of the acid is due to its addition and subsequent removal: O:C·CH → OH·CBr·CH → OH·C:C.

The frequency of the molecular change has been calculated by Dimroth's method, and the conclusion is drawn that the ultraviolet absorption bands characteristic of the ester cannot be due to the oscillations between the keto- and enolic forms (compare Baly and Desch, Trans., 1905, **87**, 768; Hantzsch, Abstr., 1910, i, 811).

Experiments have been made with the following tautomeric substances, the numbers indicating the % of enol present in the liquid at the ordinary temperature: Methyl acetoacetate 4·1, methyl methylacetoacetate 3·16, ethyl bromoacetoacetate 4·0, methyl benzoylacetate 16·3, ethyl benzoylacetate 31·9, ethyl acetonedicarboxylate 16·8, acetylacetone 80·4, benzoylacetone (solid) 99, dibenzoylmethane (solid), 102. J. J. S.

Some Reactions of Calcium Oxalate. William Oechsner de Coninck and A. Raynaud (*Bull. Soc. chim.*, 1911, [iv], **9**, 301—306).—Calcium oxalate, CaC_2O_4,H_2O, undergoes the following reactions: On gentle warming chlorine reacts quantitatively, giving calcium chloride and carbon dioxide. Bromine and iodine react similarly. On warming with concentrated hydrochloric acid, it dissolves completely, a small quantity of carbon dioxide being evolved only on boiling. With dry hydrogen chloride at a red heat, carbon monoxide and dioxide are evolved. Hydrobromic acid and hydrogen bromide react similarly to the chlorine compounds. Concentrated nitric acid reacts according to the equation: $CaC_2O_4 + 3NHO_3 = Ca(NO_3)_2 + NO_2 + H_2O + 2CO_2$. Concentrated sulphuric acid gives the ordinary reaction with oxalates.

Calcium oxalate loses its water of crystallisation only at temperatures above 100°; towards a red heat, carbon dioxide commences to be evolved, carbon being liberated at the same time. At a bright red heat, carbon monoxide is evolved, the evolution of gas taking place suddenly. Sodium and potassium oxalates behave similarly towards heat.

The action of a red heat on mixtures of calcium oxalate with various oxides has been studied. With silica, carbon dioxide only is evolved and calcium silicate formed, either SiO_2,CaO or $3SiO_2,2CaO$, or a mixture of both, according to the proportions taken. Boron trioxide gives carbon dioxide and a calcium borate of indefinite composition. Titanium dioxide gives carbon dioxide and a residue of indefinite composition. Uranium trioxide hydrate, UO_3,H_2O, gives calcium carbonate, carbon dioxide, and uranium dioxide; the green oxide of uranium, U_3O_8, acts similarly. With stannic oxide a mixture of carbon monoxide

and dioxide is evolved, leaving a residue of calcium stannate and calcium oxide. Ferric oxide, as also black oxide of iron, Fe_3O_4, gives calcium carbonate, ferrous oxide, and carbon dioxide. With lead dioxide, carbon dioxide is evolved, a mixture of calcium oxide, red lead, and litharge remaining. Red lead reacts similarly, the lead compound remaining being litharge. Manganese dioxide gives carbon dioxide, calcium oxide, and the oxide Mn_3O_4. Antimonious oxide is reduced to antimony, carbon dioxide being evolved and calcium oxide formed. Bismuth oxide is similarly reduced to the oxide BiO.

Careful heating of a mixture of calcium oxalate and barium peroxide gives a residue of calcium oxide, barium oxide, and barium carbonate, carbon dioxide being evolved. T. S. P.

Yttrium Potassium Oxalate. L. A. PRATT and CHARLES JAMES (*J. Amer. Chem. Soc.*, 1911, **33**, 488—492).—Cleve and Höglund (this Journ., 1873, 136) described two yttrium potassium oxalates, $Y_2(C_2O_4)_3,4K_2C_2O_4,12H_2O$ and $Y_2(C_2O_4)_3,K_2C_2O_4,H_2O$.

A study has been made of the solubility of yttrium oxalate in potassium oxalate solutions at 25°, and the accompanying solid phases have been examined. Varying quantities of potassium and yttrium oxalates were shaken with 75 c.c. of water until equilibrium was established. The results of the experiments are tabulated and plotted as curves. It has been found that the only yttrium potassium oxalate formed at 25° is the salt, $Y_2(C_2O_4)_3,4K_2C_2O_4,12H_2O$. This compound can exist in contact with an aqueous solution of potassium oxalate containing more than 27·5 grams of the oxalate per litre. E. G.

Condensations in the Mesoxalic Ester Series. RICHARD S. CURTISS and EARLE K. STRACHAM (*J. Amer. Chem. Soc.*, 1911, **33**, 396—400).—In an earlier paper (Curtiss and Spencer, Abstr., 1909, i, 763), an account has been given of the preparation and reactions of methyl oxomalonate. A study has now been made of the corresponding ethyl ester.

Ethyl oxomalonate, $CO(CO_2Et)_2$, b. p. 117°/31 mm., obtained by distilling ethyl dihydroxymalonate with phosphoric oxide, is a green oil, which has D_{20}^{20} 1·119, and, when cooled with a mixture of solid carbon dioxide and ether, crystallises in aggregates of radiating, colourless plates, m. p. below −30°. When the ester is treated with hydrogen chloride at −60° to −70°, it is converted into a white, crystalline mass, which melts between −29° and −10° with evolution of hydrogen chloride, and consists of a mixture of additive compounds containing HCl, 2HCl, and 3HCl respectively. Hydrogen bromide unites with the ester in a similar manner. Methyl oxomalonate combines with only 1 mol. of a halogen hydride (Curtiss and Spencer, *loc. cit.*).

When ethyl oxomalonate is treated with urethane, *ethyl carbethoxyaminotartronate*, $OEt\cdot CO\cdot NH\cdot C(CO_2Et)_2\cdot OH$, m. p. 32—33°, is produced, which forms colourless crystals, and yields a *disodium* salt, probably of the enolic form. If this ester is left in contact with phosphoric oxide for twenty-four hours, a colourless, crystalline *compound*, m. p. 121·5°, is formed, which is being investigated.

Carbamide reacts with ethyl oxomalonate with production of a crystalline *substance*, m. p. 132—133°, which appears to consist of *ethyl carbamidotartronate*, $NH_2\cdot CO\cdot NH\cdot C(CO_2Et)_2\cdot OH$, together with about 5% of carbamide. E. G.

The Solution Densities of Dextrose, Lævulose, and Maltose. ARTHUR R. LING, LEWIS EYNON, and JOSEPH H. LANE (*7th Intern. Congr. Appl. Chem.*, London, 1909, Sect. I., 137—138).—The specific gravities of solutions of dextrose, lævulose, and maltose are tabulated for concentrations from 1 to 24%, specially purified sugars having been used for the determinations. C. H. D.

Digestive Ferments for Hexotrioses and for Stachyose. HENRI BIERRY (*Compt. rend.*, 1911, **152**, 904—906. Compare this vol., i, 263).—Although the enzymes of the digestive system of vertebrates are without action on trioses, these sugars are hydrolysed with facility by ferments present in the gastro-intestinal juice of molluscs and crustaceans. The juice from *Helix* and *Astacus* hydrolyses raffinose, gentianose, rhamninose, and the tetrose stachyose. W. O. W.

***iso*Rhodeose.** EMIL VOTOČEK (*Ber.*, 1911, **44**, 819—824. Compare Abstr., 1910, i, 223, 274).—*iso*Rhodeose from purgic acid has the annexed constitutional formula, and is the optical antipode of Fischer's *iso*rhamnose. On oxidation with nitric acid, the same trihydroxyxyloglutaric acid is formed as is obtained from *iso*rhamnose. Crystalline *iso*rhodeose has $[\alpha]_D$ +31·5° (*iso*rhamnose having $[\alpha]_D$ −30°); it does not form insoluble hydrazones.

$$\begin{array}{rcccccl} & H & & OH & & H & \\ CH_3\cdot CH(OH)\cdot & C & — & C & — & C & \cdot CHO \\ & OH & & H & & OH & \end{array}$$

*iso*Rhodeosephenylosazone has m. p. 186—187°; 0·2 gram dissolved in 10 c.c. of a mixture of pyridine and alcohol in a 100 mm. tube has α −2·9°; under similar conditions the phenylosazone of rhamnose (identical with that of *iso*rhamnose) has α −3·5°. *iso*Rhodeose-*p*-bromophenylosazone has m. p. 221·5—222°.

Further proof of the constitution is afforded by the oxidation of *iso*rhodeose to *iso*rhodeonic acid, conversion of this into *anti*rhamnonic acid by means of pyridine, reduction to *anti*rhamnose, addition of hydrogen cyanide, forming *anti*rhamnohexonic acid, and oxidation of this to mucic acid. The intermediate products were not isolated, but mucic acid was identified. E. F. A.

Photochemical Synthesis of Carbohydrates. I. Sorbose. GIUSEPPE INGHILLERI (*Zeitsch. physiol. Chem.*, 1911, **71**, 105—109).—Tubes containing 40% formaldehyde and crystallised oxalic acid were exposed to sunlight for fourteen months. The product contained a carbohydrate, which separated in regular orthorhombic crystals, m. p. 98°, and formed a phenylosazone crystallising in dark yellow, stellate crystals, m. p. 164°. The phenylmethylosazone was dark yellow. The carbohydrate was optically inactive; it is assumed to be sorbose. E. F. A.

Stereochemical Configuration of the Sugars Fucose and Rhodeose. C. S. Hudson (*J. Amer. Chem. Soc.*, 1911, **33**, 405—410).—The constitution and configuration of fucose and rhodeose have been established by Mayer and Tollens (Abstr., 1907, i, 588) and Votoček (Abstr., 1906, i, 378, 483; 1910, i, 223).

In an earlier paper (Abstr., 1910, i, 220), the author has pointed out a relation between the constitution and optical rotatory power of the sugar lactones, and has shown that it can be applied to the determination of the constitution of the sugars. By means of this relation, it is now shown that, since rhodeonic and rhodeohexonic lactones are strongly lævorotatory (Krauz, Abstr., 1910, i, 224), rhodeose and fucose must have the configurations which have already been assigned to them. E. G.

Colorimetric Method of Determining the Molecular Size of Polysaccharides. Leonhard Wacker (*Zeitsch. physiol. Chem.*, 1911, **71**, 143—152. Compare Abstr., 1908, i, 135; 1909, i, 633).—The intensity of the colour given by carbohydrates with *p*-phenylhydrazinesulphonic acid in presence of sodium hydroxide, when that of dextrose is 100, varies after inversion from 107·1 in the case of a carbohydrate with three hexoses to 110·9 in that of a polysaccharide with one hundred hexoses. The mean value is 109, and this divided by the colour intensity shown by the polysaccharide before inversion by acid gives the number of hexoses in the molecule. Lævulose and carbohydrates yielding lævulose on hydrolysis give a somewhat deeper coloration. The influence of acids and alkali on the intensity of the colour for the various sugars is shown to be negligible.

The method shows erythro- and acro-dextrin to contain four hexoses; starch, seven hexoses, and glycogen, eight or nine hexoses.

E. F. A.

Cellulose. Hydrocellulose. H. Jentgen (*Zeitsch. angew. Chem.*, 1911, **24**, 585—586).—A reply to Schwalbe (this vol., i, 115).

T. S. P.

Mercerisation of Cellulose. Oswald Miller (*Ber.*, 1911, **44**, 728—731).—Mainly a reply to the criticisms of Cross (this vol., i, 114) of previous work of the author (this vol., i, 17).

The fact that mercerised cellulose, when kept over fused calcium chloride at 23—25°, loses its water at a gradually diminishing rate, supports the view that mercerised cellulose is not a hydrate, but contains adsorbed water. F. B.

Nitrous Esters of Cellulose. M. Marqueyrol and D. Florentin (*Bull. Soc. chim.*, 1911, [iv], **9**, 306—309).—The experimental evidence given by Nicolardot and Chertier (Abstr., 1910, i, 818) in support of the existence of nitrous esters of cellulose is not satisfactory for several reasons: (*a*) It is improbable that nitrous esters could be formed in a nitric acid medium. (*b*) It is well known that nitrated celluloses with a low nitrogen content are insoluble in the usual solvents for guncotton, namely, ethyl acetate, acetone, etc. (*c*) Various investigators have shown that the nitric esters of cellulose

when saponified with aqueous or alcoholic alkali give rise to considerable quantities of nitrite, since reduction accompanies the saponification.

It is furthermore shown that if cellulose is nitrated by the prolonged action of nitric acid ($D_4^{15} = ca.\ 1{\cdot}5$) to which excess of carbamide has been added to destroy all the nitrous acid present, or formed during the reaction, products are obtained which cannot be nitrous esters, but which nevertheless possess the properties ascribed to these compounds by Nicolardot and Chertier. T. S. P.

Action of Ultra-violet Radiations on Starch. L. Massol (*Compt. rend.*, 1911, **152**, 902—904).—Soluble starch becomes hydrolysed when its aqueous solution is exposed to the light from a quartz-mercury lamp. Changes in the rotatory power of the solution show that the transformation is probably into dextrins and maltose, although the amount of sugar isolated was insufficient for identification. The hydrolysis is not due to the small amount of hydrogen peroxide formed under the action of the rays. W. O. W.

Catalytic Transformation of Starch Paste. Auguste Fernbach and Jules Wolff (*7th. Intern. Congr. Appl. Chem.*, 1909, Sect. VI B, 124—128).—When to 50 c.c. of 5% starch-paste a few drops of hydrogen peroxide (corresponding with 5 mg. of oxygen) and of a ammonia solution (corresponding with 4 mg. of ammonia) are added, the paste rapidly becomes liquid, and in about fifteen minutes has a viscosity comparable to that of water. Other alkalis act similarly; there appears to be an optimum quantity of these, and, if excess is added, the liquefaction is retarded. There is partial neutralisation of the alkali during the change corresponding with 1·6 mg. of ammonia per gram of starch. A similar liquefying effect is exercised by hydrogen peroxide and certain salts (Wolff, Abstr., 1908, i, 137).

The optimum reaction in presence of fixed quantities of hydrogen peroxide and ferrous sulphate takes place when sodium hydroxide is added until the mixture is very faintly alkaline to methyl-orange. The slightest excess of acid very materially retards the liquefaction. Lactic and succinic acids in equivalent proportions are only one-third as harmful as succinic acid.

Ferric sulphate has only one-half to one-third the activity of ferrous sulphate. Copper sulphate is about twice as active as ferrous sulphate, and its effect is less susceptible to the presence of acids, sodium hydroxide having no influence. Manganese sulphate is very slightly active. Mono- and di-sodium phosphate retard the change, particularly the latter.

The minimum quantity of hydrogen peroxide in time brings about liquefaction, provided the reaction remains neutral or feebly alkaline, but this is probably due to the influence of impurities in the starch.

When a large proportion of hydrogen peroxide is used at 70—75°, the starch after two hours no longer gives an iodine coloration, the liquid has a marked reducing power, and is acid. The reducing substance is insoluble in alcohol, and is precipitated from a concentrated solution by copper sulphate. E. F. A.

Characteristic Properties of Amylose and Amylopectin. Mme. Z. GATIN-GRUZEWSKA (*Compt. rend.*, 1911, **152**, 785—788. Compare Abstr., 1908, i, 320; Maquenne, *ibid.*).—The envelope of a potato-starch grain consists of amylopectin associated with inorganic substances. Neither crude nor pure amylopectin shows the phenomenon of ageing or spontaneous precipitation from solution on cooling (Maquenne and Roux's retrogradation). On the other hand, amylose has this property, the precipitation being more complete the purer the substance. When starch paste is cooled, the hydrosol granules of amylose are precipitated, and carry with them the gel of amylopectin, in which they are suspended. W. O. W.

Oxidation of Humic Acid. A. G. DOJARENKO (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. VII., 11—18).—When humic acid is oxidised with 30% hydrogen peroxide, a part of the nitrogen is detached in the forms of ammonia and soluble amides and amino-acids. The amide- and amino-acid nitrogen pass into the oxidised form of humus compounds, perhaps *apo*crenic acid, whilst the rest of the nitrogen of humic acid, the "humin nitrogen," serves as source of ammonia and simple amides. The properties of humic acid, as regards the production of assimilable nitrogen when oxidised, can be ascertained from the amounts of the different forms of nitrogen, especially the amount of "humin nitrogen."

The solution of humic acid in alkalis results in the production of *apo*crenates and crenates, and also in the breaking off of nitrogen in the form of ammonia and other simple compounds. The former are derived from amide- and amino-acid nitrogen, whilst the "humin nitrogen" yields the less complex nitrogen compounds.

N. H. J. M.

Preparation of Ethyl Oxalhydrazinate. ROBERT STOLLÉ (*Ber.*, 1911, **44**, 776—777).—*Ethyl oxalhydrazinate*, $CO_2Et\cdot CO\cdot NH\cdot NH_2$, is formed by the action of hydrazine hydrate on an alcoholic solution of ethyl oxalate at $-10°$ to $-15°$, and is most readily isolated as its *benzylidene* derivative, $CO_2Et\cdot CO\cdot NH\cdot N\colon CHPh$, which crystallises from alcohol in colourless, refractive needles, m. p. 133°. The *oxalate*, $CO_2Et\cdot CO\cdot NH\cdot NH_2,H_2C_2O_4$, crystallises from hot alcohol, and reduces hot Fehling's solution. J. J. S.

Sodium Derivatives of Bromo-amides and their Rôle in Hofmann's Reaction. CHARLES MAUGUIN (*Ann. Chim. Phys.*, 1911, [viii], **22**, 297—369. Compare Abstr., 1909, i, 892).—A further study of these compounds, the preparation of which has already been described. Owing to their explosive character, the preparation is not free from danger.

When bromoacetamide is prepared by Hofmann's method, the product consists of a mixture of the anhydrous compound (slender needles, m. p. 106°) with a monohydrate. The latter separates from warm solutions in orthorhombic, hemimorphic crystals (compare François, Abstr., 1909, i, 13, 140). *Bromoisobutyramide*, prepared by

adding bromine (2 mols.) and potassium hydroxide (1 mol.) to the amide (2 mols.) in chloroform at −15°, forms monoclinic needles, m. p. 92°.

The sodium derivatives of bromoamides react with urethanes in benzene solution, giving substituted allophanates of the type

$NHR{\cdot}CO{\cdot}NH{\cdot}CO_2R'$,

termed by the author ureocarbonic esters (compare Diels and Jacoby, Abstr., 1908, i, 613). Thus urethane and sodium bromoacetamide form *ethyl methylcarbamidecarboxylate*, $NHMe{\cdot}CO{\cdot}NH{\cdot}CO_2Et$, needles, m. p. 134°; this compound was also obtained by the action of ethyl chlorocarbonate on methylcarbamide. The *methyl* ester crystallises in lamellæ, m. p. 163°; the *propyl* ester has m. p. 130°. Sodium bromopropionamide gives *methyl ethylcarbamidecarboxylate*,

$NHEt{\cdot}CO{\cdot}NH{\cdot}CO_2Me$,

needles subliming at 40—50°, m. p. 95°; the ethyl ester has m. p. 72° (Jacoby, Thesis, 1907, gives 64—65°); the *propyl* ester has m. p. 81°; the iso*butyl* ester, lamellæ, m. p. 87°; the iso*amyl* ester, needles, m. p. 67—68°. *Methyl* iso*propylcarbamidecarboxylate* forms monoclinic prisms, m. p. 70°; the *ethyl* ester, m. p. 40°.

Amides react with their sodium bromo-derivatives, forming ureides of the type $NHR{\cdot}CO{\cdot}NH{\cdot}COR$; thus acetamide yields acetylmethylcarbamide. Butyramide furnishes a mixture of acetylmethylcarbamide, butyrylpropylcarbamide and *acetylpropylcarbamide*, $NHPr^{\alpha}{\cdot}CO{\cdot}NHAc$, micaceous lamellæ, m. p. 115°.

When oxamethane is warmed with an aqueous solution of potassium bromoacetamide there is formed urethane, ethyl allophanate, and the *potassium* salt of a new ureide, $CO_2Et{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CO_2K$, crystallising in slender needles. The *copper* and *silver* salts are sparingly soluble; on treating the latter with ethyl iodide, the *ester*,

$CO_2Et{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CO_2Et$,

was obtained. This substance occurs in brilliant needles, m. p. 146°; its constitution was established by a study of its behaviour towards water, alcohol, and ammonia, as well as by the action of these substances on the potassium salt. The latter is decomposed by water, giving potassium oxalate and ethyl allophanate.

Ethyl malonate and sodium bromoacetamide react to form acetylmethylcarbamide and ethyl ethylenetetracarboxylate.

The paper contains crystallographic details, illustrated by diagrams, of most of the substances mentioned. W. O. W.

The Catalytic Action of Potassium Carbonate on the Absorption of Nitrogen by Calcium Carbide. GINO POLLACCI (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. II, 278—282).—It is known that the absorption of nitrogen by calcium carbide is accelerated by calcium fluoride (Foerster and Jacoby, Abstr., 1907, i, 397) and by various chlorides (Bredig, Fraenkel, and Wilke, *ibid.*, 396, 903). It is now found that potassium carbonate has an accelerating action, lowering the temperature at which absorption takes place, the best result being obtained when 4% of potassium carbonate is added. There is no advantage in raising the pressure of the nitrogen above one atmosphere. C. H. D.

Action of Nitrous Acid on Aminoguanidine and on Semicarbazide. Difference between the Tetrazen, $C_2H_8ON_2$, and Azoimides in their Behaviour Towards Hydriodic Acid. KARL A. HOFMANN, HEINRICH HOCK, and HEINRICH KIRMREUTHER (*Annalen*, 1911, 380, 131—147).—The compound obtained by the action of sodium nitrite on a solution of aminoguanidine dinitrate, and termed aminoguanidine diazohydroxide (Abstr., 1910, i, 232) or guanyldiazoguanyltetrazen (*ibid.*, 446), is formed in larger quantity when an excess of sodium nitrite is used. The compound cannot contain the hydrate of an azoimide, $NH:\underset{|}{C}\cdot N_3, H_2O$, as carbamideimideazoimide, $NH_2\cdot C(:NH)\cdot N_3$, and carbamic acid azoimide, $NH_2\cdot CO\cdot N_3$, are readily decomposed by acids, alkalis, and silver salts, yielding hydrazoic acid.

Hydriodic acid reacts with hydrazoic acid and azoimides, yielding nitrogen, amine, and free iodine, $N_2:NR + 2HI = N_2 + NH_2R + I_2$, but with the derivative from aminoguanidine the acid merely forms the pale yellow iodide, or with a mixture of hydrochloric and hydriodic acids the chloroperiodide, $(C_2H_{10}N_7)_2ClI_3$. The compound is thus a base, and yields salts by the introduction of acid in place of water. It is regarded as a β-nitrosohydrazine derivative with the formula: $NH_2\cdot C(NH)\cdot NH\cdot NH\cdot N:N\cdot C(:NH)\cdot NH\cdot NH\cdot NO$, and in the formation of salts water is eliminated and a terminal diazo-group is formed. The nitroso-compound (tetrazen) is extremely stable, and is not attacked by sodium acetate solution, nitrous acid, sodium hydrogen sulphite, ammonium hydrogen sulphide, hydroxylamine, hydrazine sulphate, phenylhydrazine, hydrogen peroxide, formaldehyde, acetone, benzaldehyde, aniline, pyridine, or acetic anhydride. When reduced with stannous chloride and hydrochloric acid, it yields tetrazylhydrazine, which is isolated as its benzylidene derivative (Thiele, Abstr., 1893, i, 441). The sulphate, $(C_2H_7N_{10})_2SO_4$, crystallises in long, colourless prisms, and is hydrolysed by water; the acid sulphate yields the double *sulphate*, $C_2H_7N_{10}\cdot SO_4H, Ag_2SO_4$, in the form of glistening, doubly refractive needles. The *double* salt, $C_2H_7ON_{10}Ag, AgNO_3, 3H_2O$, crystallises in pale yellow, glistening needles, and when boiled with dilute hydrochloric acid evolves nitrogen (3 atoms). With ammonia, the silver salt yields silver cyanamide and the silver derivative of tetrazylazoimide.

The *iodide*, $C_2H_7N_{10}I$, forms pale yellow, flat needles, only slightly pleochroic, and is extremely explosive. The *periodide*, $C_2H_7N_{10}I_5$, forms glistening, greenish-black, rhombohedral crystals, and the *chloroiodide*, $(C_2H_7N_{10})_2ClI_3$, forms pointed prisms, strongly pleochroic, from pale yellow to deep black, and also doubly refractive.

Semicarbazide hydrochloride and sodium nitrite yield the azoimide of carbamic acid, which is decomposed by copper acetate solution, yielding hydrazoic acid in the form of the *double* salt, $N_3\cdot Cu\cdot C_2H_3O_2$. This forms long, dark green needles, and when kept under water yields copper hydrazoate.

Semicarbazide hydrochloride and sodium nitrite in the presence of sodium acetate yield hydrazoic acid hydrazodicarbonamide (Thiele, Abstr., 1892, 1298), as represented by the equation:

$$NH_2\cdot CO\cdot NH\cdot NH_2 + NO\cdot OH + NH_2\cdot NH\cdot CO\cdot NH_2 = NH_2\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2 + N_3H + 2H_2O.$$

The formation of guanylnitrosoguanyltetrazen from aminoguanidine dinitrate and sodium nitrite probably proceeds in a similar manner.

J. J. S.

Reaction of Iodoacetonitrile with Silver Nitrate. S. K. Loy and Salomon F. Acree (*Amer. Chem. J.*, 1911, **45**, 224—230).—It has been stated by Acree and Shadinger (Abstr., 1908, ii, 163) that in the reactions between urazoles and alkyl halides, it is probable that, in some cases, the anion first unites with the alkyl halide to form an unstable complex anion, which then decomposes, thus:

(1) $CH_3I + Ag^{\cdot} + NO'_3 \rightleftarrows CH_3I,NO'_3 + Ag^{\cdot} \longrightarrow CH_3{\cdot}NO_3 + Ag^{\cdot} + I'$.

(2) $CH_3I + AgNO_3(\text{or } Ag^{\cdot} + NO'_3) \rightleftarrows CH_3I,AgNO_3 \longrightarrow CH_3{\cdot}NO_3 + AgI$.

It was shown that in certain urazole reactions not more than traces of the complex salt could be present. In order to obtain evidence as to the existence of appreciable quantities of such a salt in solution, a study has been made of the double compound, $AgNO_3,CH_2I{\cdot}CN$, obtained by Scholl and Steinkopf (Abstr., 1907, i, 116) by the action of silver nitrate on iodoacetonitrile. Assuming that the complex salt is not more highly ionised than silver nitrate, and that the complex ion $NO'_3{\cdot}ICH_2{\cdot}CN$ must migrate more slowly than the NO'_3 ion, it follows that if the complex salt is actually formed and decomposes slowly enough to be studied, the conductivity of a standard solution of silver nitrate should be reduced on the introduction of acetonitrile to a degree depending on the amount of complex salt formed.

Measurements have therefore been made of the conductivity of aqueous mixtures of silver nitrate and iodoacetonitrile in comparison with solutions of silver nitrate of the same concentration. The conductivities have also been determined of solutions in methyl alcohol, ethyl alcohol, and acetone. The results show that the double compound, $AgNO_3,CH_2I{\cdot}CN$, does not exist to any appreciable extent in such mixtures, and its rapid precipitation from solutions of its components must therefore be due to its small solubility and not to its appreciable concentration at any moment.

E. G.

Direct Preparation of Metallic and Organic Sulphonates from Crude Sulphonation Products. Alphonse Seyewetz and L. Poizat (*Bull. Soc. chim.*, 1911, [iv], **9**, 247—253).—An extension of Gattermann's method (Abstr., 1891, 1226) for the preparation of sulphonates without the intervention of the barium salt.

The precipitation of sodium salts of sulphonic acids when sodium chloride is added to crude sulphonation products is due to the slight solubility of these salts in the excess of sulphuric acid present. This property is shown by all salts of sodium, which are decomposed by sulphuric acid and by similar salts of the alkali and other metals, and also of certain organic bases, and a large number of metallic benzenesulphonates have been prepared by this method and are described in this paper.

Hydroxylamine benzenesulphonate, colourless leaflets, and p-*aminophenyl benzenesulphonate*, colourless needles or leaflets, were also obtained in like manner. The corresponding *salts* of *phenylhydrazine*, m. p. 176°, and of *carbamide*, m. p. 162—163°, were obtained by

adding the respective bases suspended in water to the crude sulphonation product; both are crystalline. These four salts are best purified by crystallisation, first from water and then from alcohol.

T. A. H.

Conversion of Benzenesulphondibromoamide into Dibromobenzenesulphonamide by means of Concentrated Sulphuric Acid. JOSEPH H. KASTLE (*Amer. Chem. J.*, 1911, **45**, 219—223).—It has been shown by Benedikt (Abstr., 1879, 717) that when tribromophenol bromide is treated with concentrated sulphuric acid, it is converted into tetrabromophenol.

Since benzenesulphondibromoamide shows many analogies to tribromophenol bromide, it was considered of interest to ascertain whether it is similarly transformed by sulphuric acid. It has been found that a reaction occurs instantly at the ordinary temperature with liberation of traces of bromine and formation of a dibromobenzenesulphonamide, m. p. 194°, which is probably the *p*-dibromo-compound. A small quantity of another substance, m. p. 135—140°, is simultaneously produced, which contains 36% of bromine, but has not yet been identified.

E. G.

Triphenylmethyl. XX. MOSES GOMBERG and DONALD D. VAN SLYKE (*J. Amer. Chem. Soc.*, 1911, **33**, 531—549).—In earlier papers (Gomberg, Abstr., 1907, i, 504; 1909, i, 144) it has been stated that triphenylmethane compounds exist in both benzenoid and quinonoid forms. The present work was undertaken with the object of ascertaining whether ortho-quinonoid nuclei occur in the products of tautomerisation, or whether only para-quinonoid rings are formed. If the former is the case, the halogen atom should be just as reactive in the ortho-position as it has been found to be in the para-position in the tautomerised products, whilst if the *o*-halogen is inert it may be concluded that ortho-quinonoid modifications are not produced.

o-*Chlorotriphenylcarbinol*, $C_6H_4Cl{\cdot}CPh_2{\cdot}OH$, m. p. 95°, obtained by the action of ethyl *o*-chlorobenzoate on magnesium phenyl bromide, forms white crystals; the *chloride* has m. p. 136°, and the *ethyl ether*, m. p. 77°. o-*Chlorotriphenylmethylaniline*, $C_6H_4Cl{\cdot}CPh_2{\cdot}NHPh$, has m. p. 121°. o-*Chlorotetraphenylethane*, $C_6H_4Cl{\cdot}CPh_2{\cdot}CH_2Ph$, prepared by Gomberg and Cone's method (Abstr., 1906, i, 414), has m. p. 165·5°.

o-*Bromotriphenylcarbinol*, $C_6H_4Br{\cdot}CPh_2{\cdot}OH$, m. p. 104°, obtained by the action of ethyl *o*-bromobenzoate on magnesium phenyl bromide, forms white crystals; the *chloride* was also prepared. The *ethyl ether* has m. p. 69—70°. o-*Bromotriphenylmethylaniline*,

$$C_6H_4Br{\cdot}CPh_2{\cdot}NHPh,$$

has m. p. 126°, and o-*bromotetraphenylethane*, $C_6H_4Br{\cdot}CPh_2{\cdot}CH_2Ph$, m. p. 153°.

Di-p-*chloro*-o-*bromotriphenylcarbinol*, $C_6H_4Br{\cdot}C(C_6H_4Cl)_2{\cdot}OH$, m. p. 107°, obtained by the action of magnesium *p*-chlorophenyl iodide on ethyl *o*-bromobenzoate, forms white crystals; the *chloride* has m. p. 165°, and the *ethyl ether*, m. p. 107°. *Di*-p-*chloro*-o-*bromotriphenylmethylaniline*, $C_6H_4Br{\cdot}C(C_6H_4Cl)_2{\cdot}NHPh$, has m. p. 212°, and *di*-

p-*chloro*-o-*bromotetraphenylethane*, $C_6H_4Br\cdot C(C_6H_4Cl)_2\cdot CH_2Ph$, m. p. 162°.

Di-p-*chloro*-p-*bromotriphenylcarbinol*, $C_6H_4Br\cdot C(C_6H_4Cl)_2\cdot OH$, has m. p. 106°; the chloride has already been described (Abstr., 1907, i, 506); the *ethyl ether* has m. p. 188°. *Di*-p-*chloro*-p-*bromotriphenylmethylaniline*, $C_6H_4Br\cdot C(C_6H_4Cl)_2\cdot NHPh$, has m. p. 182°.

The action of molecular silver on the halogen-substituted triphenylmethyl chlorides has been studied, with the following results (compare Gomberg and Cone, Abstr., 1906, i, 824). Not a trace of the halogen in the ortho-position was removed in any case, and there is therefore no indication of the formation of an *o*-quinonoid nucleus. The total amounts of halogen in the para-position removed, in relation to the number of *p*-halogen atoms present, are in accord with Gomberg and Cone's results. Bromine in the para-position is more reactive towards molecular silver than is chlorine. The colorations produced by the action of molecular silver on the *o*-halogen derivatives are deeper and more brilliant than those produced with the corresponding para-derivatives.

Experiments have been made to ascertain the action of silver sulphate on ortho- and para-halogen derivatives of triphenylmethyl chloride, and Gomberg's conclusion (Abstr., 1907, i, 505) that the coloured triphenylmethyl sulphates have a quinonoid structure is confirmed. One para-halogen atom, and one only, becomes unstable, and can be readily removed by further action of the silver. The ortho-halogen atoms are not affected. When one or two nuclei contain bromine and the other nucleus or nuclei chlorine, all in the para-position, the transformation of the sulphate into the quinonoid form in methyl sulphate solution takes place almost entirely in the brominated nuclei.

The para-halogen atoms in the acid sulphates, unlike those in the normal sulphates, cannot be removed by the action of silver sulphate, owing to the sulphuric acid in the acid sulphates being directly combined with the para-halogen of the quinonoid nucleus.

When *o*-bromo- and di-*p*-chloro-*o*-bromo-triphenylmethyl chlorides are treated with sulphur dioxide and silver chloride in sealed tubes, no silver bromide is produced in either case.

There was not any evidence of the formation of *o*-quinonoid nuclei in any of the experiments with the *o*-bromo-derivatives, and the conclusion is therefore drawn that only *p*-quinonoid rings are formed.

E. G.

Decacyclene and its Alleged Property of Dissolving Graphite. MAURICE PADOA (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 345—347).—The yield of decacyclene by the method of Dziewonski (Abstr., 1903, i, 431) is poor. If, however, the sulphur and acenaphthene are heated together in a sealed tube for two hours at 200°, the high pressure then reduced, and the heating resumed for an hour at 250°, a yield of 12 grams of decacyclene is obtained for every 100 grams of acenaphthene. From an observation of the cooling curve, the m. p. was found to be 389·5°.

When in repetition of Ostromisslensky's experiment (Abstr., 1907, ii, 864) the hydrocarbon was heated at 500° for an hour with various samples of graphite, decomposition occurred. If a lower temperature was employed (430°), the cooling curve was that of the pure substance, and the graphite was recovered unchanged. R. V. S.

Colorations Produced by the Interaction of Aromatic Amino- and Nitro-compounds. JOHANN WALTER (*Zeit. Farb.-Ind.*, 1911, Reprint).—A description is given of the colorations produced when commercial dimethylaniline is treated with picric acid, styphnic acid, nitronaphthalene, nitrobenzene, *m*-dinitrobenzene, *o*- and *p*-nitrotoluenes, and dinitro-α-naphthol. Nitronaphthalene is coloured reddish-orange by dimethylaniline (or, better, by dimethyl- or diethyl-*p*-toluidine), the solution being yellow or orange-yellow; the reaction possibly could be used to detect the addition of nitronaphthalene to oils.

The colorations produced by the following aromatic bases on filter-paper soaked in a solution of trinitrotoluene in toluene and dried are described: dimethylaniline, aniline, *o*-toluidine, *p*-toluidine, ethylaniline, benzylethylaniline, dimethyl-α-naphthylamine, diethylaniline, amylaniline, dimethyl-*p*-toluidine, diethyl-*p*-toluidine, dimethyl-*o*-toluidine, nitrosodimethylaniline, diphenylamine, quinoline, tetramethyldiaminodiphenylmethane, tetramethyldiaminobenzophenone, diaminotriphenylmethane, tetramethyldiaminotriphenylmethane, hexamethyltriaminotriphenylmethane, α-naphthylamine, β-naphthylamine, anthranilic acid, *p*-aminobenzoic acid, dimethyl-*p*-aminobenzoic acid and its amide, anilide, and ethyl ester, *o*-tolylglycine, ethyl phenylglycine, phenylaminoacetonitrile, diethyl-*m*-aminophenol, *m*-aminophenol, indigotin, and tetramethyl-*m*-phenylenediamine. The prepared filter-paper did not give colorations with acridine, indolecarboxylic acid, phthalimide, benzamide, acetamide, acetanilide, carbamide, and bisphenylmethylpyrazolone.

Many of the preceding substances are only the commercial preparations; consequently, too much reliance must not be placed on the colorations. By a systematic study and comparison of the colorations produced by pure materials, the author thinks it should be possible to ascertain the presence of definite groups, their position, and method of union in substances of unknown or doubtful constitution. One or two interesting suggestions are made in the paper. The use of ether in the extraction of large volumes of dilute aqueous solutions of certain substances (dimethylaniline is the instance quoted) may be avoided by shaking the solution with trinitrotoluene, filtering, and decomposing the precipitate with dilute acid, whereby the substance is isolated (after basification, if necessary).

Dimethylaniline or dimethyl- or diethyl-*p*-toluidine probably could be used to detect trinitrotoluene in explosives.

When a solution of dimethylaniline in benzene is distilled on the water-bath, the presence of dimethylaniline in the distillate can be shown by the yellow coloration produced by trinitrotoluene. This proves that the solvent recovered by the distillation of a solution

in a solvent of low b. p. is not pure, as is frequently assumed to be the case.

The naphthionic acid used in the preparation of dyes must be of good quality and free from *a*-naphthylamine in particular; the presence of the latter can be detected by the brownish-red coloration produced by trinitrotoluene paper. C. S.

Quantitative Investigations on the Nitration of Aniline. ARNOLD F. HOLLEMAN, J. C. HARTOGS, and T. VAN DER LINDEN (*Ber.*, 1911, **44**, 704—728).—The authors have investigated the composition of the products obtained when aniline and its acyl derivatives are nitrated under various conditions.

By nitrating aniline at $-20°$ in sulphuric acid solution, *m*- and *p*-nitroanilines are produced in approximately equal quantities; the amount of the ortho-compound varies from 1—2%. When the nitration is effected by adding aniline nitrate to sulphuric acid, the amount of *m*-nitroaniline diminishes, whilst that of the ortho- and para-isomerides increases.

Formanilide, when nitrated with pure nitric acid, yields 2:4-dinitroformanilide; with 80% nitric acid the product consists of *o*- and *p*-nitroformanilides, the latter being present in the greater proportion; on nitration at $-20°$ with the calculated amount of nitric acid in sulphuric acid solution, the product consists almost exclusively of the para-isomeride. Similar results were obtained in the nitration of acetanilide and of benzanilide.

The product obtained by nitrating acetanilide with acetyl nitrate at $-25°$ consists of 76·7% of ortho-, 4·1% of meta-, and 20·2% of para-nitroacetanilide; the relative proportions are very similar when the nitration is carried out in carbon tetrachloride solution.

Since the concentration of the nitric acid employed has a considerable influence on the relative proportions of the isomerides, the effect of partly or wholly replacing the water by acetic acid was studied. In the case of acetanilide partial replacement of the water by acetic acid causes an increase in the amount of the para- and a diminution in that of the ortho-isomeride. By nitrating acetanilide with pure nitric acid containing 20% of glacial acetic acid, the product consists entirely of 2 : 4-dinitroacetanilide.

By the removal of water from aniline nitrate by means of acetic anhydride at 0°, *o*-nitroaniline is formed to the extent of 82·1%, meta-2·9%, and para 15%.

The product obtained by the interaction of 74% sulphuric acid and phenylnitroamine at $-20°$ consists almost exclusively of *o*-nitroaniline.

From these results the authors draw the conclusion that by the direct nitration of aniline and its derivatives the product consists mainly of the para-compound, together with small quantities of the ortho-compound. This is, however, modified by two causes: (1) the formation of aniline sulphate and the introduction of acyl groups in the amino-group, both of which lead to the formation of the meta-substituted product; (2) the intermediate formation of phenylnitroamine, which gives rise to *o*-nitroaniline.

For the determination of the relative amounts of the three nitroanilines in a mixture, thermal methods of analysis were employed. The freezing-point curves of binary mixtures of the three nitroanilines, together with certain portions of the eutectic lines leading from the three binary eutectics to the ternary eutectic point, were first determined. The composition of a mixture of the nitroanilines was then deduced from these portions of the ternary diagram by determining the first and second freezing-points of the mixture.

Since the freezing point of any one of the nitroanilines is depressed to the same extent by the addition of equal quantities of either of the other two isomerides, the composition of a ternary mixture may be determined by adding a sufficient quantity of one of the nitroanilines to the mixture, so that this isomeride crystallises out at the initial freezing point. From the position of this point on the binary freezing-point curves, the relative amount, in the original mixture, of that isomeride which crystallises out may be calculated.

An apparatus for the determination of freezing points is described. It closely resembles Thiele's melting-point apparatus, but the open tube of the latter is inserted in one of the side limbs, which is widened and contains a test-tube in which is placed the mixture, the freezing point of which is to be determined. F. B.

Unsymmetrical Aromatic Derivatives of Oxamide. II. HERMANN SUIDA, jun. (*Monatsh.*, 1911, 32, 197—223).—In continuation of the former investigation (Abstr., 1910, i, 665), unsymmetrical oxanilides have been prepared containing the $-CO_2H$, $-NH_2$, $-OH$, and $-N\colon NPh$ groups. Also a phenyl-α-naphthyloxamide has been obtained containing a nitro-group in each nucleus. An oxanilide monosulphonate could not be obtained from ethyl oxanilate and aminobenzenesulphonate. In all cases the yields were very unsatisfactory. In some cases the desired reactions become subordinated to other reactions, for example, in the interaction of ethyl oxanilate with *p*-phenylenediamine or with *m*-aminophenol. The material so far obtained is insufficient to determine the influence of the substituents on the course of fission with alcoholic potassium hydroxide.

*Oxanilide-*o*-carboxylic acid*, $NHPh\cdot C_2O_2\cdot NH\cdot C_6H_4\cdot CO_2H,H_2O$, is obtained by heating ethyl oxanilate and anthranilic acid for three hours at 140—150°; it forms colourless, shining needles, m. p. 226—227°; the water of crystallisation is lost at 105—110°. With dichromate and sulphuric acid it gives a blood-red colour (Tafel's reaction). The *ammonium* salt is an acid salt,

$$C_{15}H_{12}O_4N_2,C_{15}H_{11}O_4N_2\cdot NH_4,$$

and loses ammonia a few degrees below 226—227°. The *potassium* salt, $C_{15}H_{11}O_4N_2K,4H_2O$, forms rhombic needles [$b:c = 1:0{\cdot}347$]. The *silver*, *calcium*, *barium*, and *copper* salts were also prepared. Under the action of alcoholic potassium hydroxide the acid decomposes into aniline and kynuric acid (oxalylanthranilic acid).

p-*Phenylazo-oxanilide*, $NHPh\cdot C_2O_2\cdot NH\cdot C_6H_4\cdot N\colon NPh$, results from the interaction of ethyl oxanilate and *p*-aminoazobenzene at 130—150°, and repeated extraction of the cold fusion with benzene. It forms ochre-yellow crystals, m. p. 256—257°, and gives a dark carmine

colour with Tafel's reaction. Alcoholic potassium hydroxide decomposes it into *p*-aminoazobenzene and oxanilic acid.

p-*Amino-oxanilide*, $NHPh\cdot C_2O_2\cdot NH\cdot C_6H_4\cdot NH_2$, could not be prepared by the reduction of either *p*-nitro-oxanilide or *p*-phenylazo-oxanilide. It is obtained by the condensation of ethyl oxanilate and *p*-phenylenediamine at 150—155° in an atmosphere of carbon dioxide. If the condensation is carried out in the air, a deep blue mass is obtained. The amino-oxanilide is obtained from this as colourless prisms and plates, m. p. 215°, by extraction with alcohol; it gives a dull carmine-red colour, with a brownish tinge, with Tafel's reaction. The *hydrochloride*, $C_{14}H_{13}O_2N_3,HCl$, and the *sulphate*, $(C_{14}H_{13}O_2N_3)_2,H_2SO_4$, are prepared by adding the respective acids to the hot alcoholic solution of the base. Alcoholic potassium hydroxide decomposes the oxanilide into aniline, *p*-phenylenediamine, oxanilic acid, and *p*-amino-oxanilic acid.

The residue insoluble in alcohol is also practically insoluble in all organic solvents, but soluble in hot concentrated sulphuric acid. It could not be identified.

By the nitration of phenyl-α-naphthyloxamide (*loc. cit.*) with concentrated nitric acid (D = 1·4), a mixture of p-*nitrophenyl*-4-*nitro-α-naphthyloxamide*, $NO_2\cdot C_6H_4\cdot NH\cdot C_2O_2\cdot NH\cdot C_{10}H_6\cdot NO_2$, and o-*nitrophenyl*-4-*nitro-α-naphthyloxamide*, is obtained. The former compound is the chief product of reaction, and can be separated from the latter by recrystallisation from glacial acetic acid; it forms slender, yellow needles, which sinter at 230° (decomp.); it does not give Tafel's reaction. The latter compound gives a dark brownish-red colour with Tafel's reaction. Fission with alcoholic potassium hydroxide gives the *p*- and *o*-nitroanilines respectively, and 4-nitro-1-naphthylamine; the acids formed at the same time could not be separated and identified.

Ethyl oxanilate and *m*-aminophenol interact readily at 150—160°. The main product of the reaction is extracted with alcohol, and gives pale rose-coloured, monoclinic tablets, m. p. 246—247°. Analysis points to the formula $4C_{14}H_{12}O_3N_2-H_2O$, that is, an anhydride compound formed from three molecules of *m*-hydroxyanilide and one molecule of oxanilide. This formula is confirmed by the preparation of a *triacetyl* derivative, $C_{64}H_{54}O_{15}N_8$, m. p. 176—178°, although the ebullioscopic determination of the molecular weight in glacial acetic acid points to the simple formula $C_{14}H_{12}O_3N_2$. With alcoholic potassium hydroxide, aniline, *m*-aminophenol, and oxalic acid are formed. On shaking with dilute aqueous sodium hydroxide, m-*hydroxyoxanilide*,

$$NHPh\cdot C_2O_2\cdot NH\cdot C_6H_4\cdot OH,$$

is continually extracted, and this compound is also obtained from the alcoholic mother liquors of the above-mentioned anhydride compound. If forms peach-red coloured leaflets, m. p. 246°, and is decomposed by alcoholic potassium hydroxide into oxanilic acid, *m*-hydroxyoxanilic acid, aniline, and *m*-aminophenol. T. S. P.

Keto-ester Additive Products with Arylamines and Alcohols. Richard S. Curtiss, Harry S. Hill, and R. H. Lewis (*J. Amer. Chem. Soc.*, 1911, **33**, 400—405).—Curtiss and Spencer

(Abstr., 1909, i, 763) have given an account of a study of the action of alcohols and amines on methyl oxomalonate. The investigation has now been extended to ethyl oxomalonate.

When ethyl oxomalonate is treated with arylamines, additive compounds of the type $R\cdot NH\cdot C(CO_2Et)_2\cdot OH$ are first produced, which are capable of undergoing further reaction with formation of compounds of the type $(NHR)_2C(CO_2Et)_2$.

In the case of aniline, evidence was obtained of the formation of the compound $NHPh\cdot C(CO_2Et)_2\cdot OH$, but this substance could not be isolated, as it immediately reacts with another molecule of aniline with production of ethyl dianilinomalonate (Curtiss, Abstr., 1897, i, 556).

o- and *p*-Toluidine react with ethyl oxomalonate to form *ethyl* o-*toluidinotartronate*, $C_6H_4Me\cdot NH\cdot C(CO_2Et)_2\cdot OH$, m. p. 92°, and *ethyl* p-*toluidinotartronate*, m. p. 95°, which crystallise in radiating needles; the *acetyl* derivative of the latter compound has m. p. 150°. *m*-Toluidine also reacts with ethyl oxomalonate, but the product was not obtained in a pure condition. When a solution of ethyl *p*-toluidinotartronate in dry ether is treated with phosphoric oxide, a thick, green oil is produced, the properties of which resemble those of methyl phenyliminomalonate (Curtiss and Spencer, *loc. cit.*); when left in the air, it absorbs moisture, and is reconverted into ethyl *p*-toluidinotartronate. Phosphorus trichloride also reacts with ethyl *p*-toluidinotartronate, with production of ethyl *p*-tolyliminomalonate,

$$C_6H_4Me\cdot N{:}C(CO_2Et)_2,$$

which is decomposed by potassium carbonate into *p*-toluidine and ethyl mesoxalate.

Benzylamine reacts with ethyl oxomalonate, but the product could not be isolated in a pure state.

When ethyl oxomalonate (1 mol.) is treated at −13° with methyl, ethyl, or benzyl alcohol (1 mol.), a colourless syrup is obtained in each case, which dissociates into the original constituents on heating, and cannot be crystallised or distilled. These compounds are doubtless *ethers* of ethyl dihydroxymalonate, $OH\cdot C(CO_2Et)_2\cdot OR$, corresponding with the product obtained by Curtiss and Spencer (*loc. cit.*) by the action of ethyl alcohol on methyl oxomalonate. E. G.

Isomerism and Polymorphism. EINAR BIILMANN (*Ber.*, 1911, **44**, 827—837).—The classification of isomerism by Kruyt (Abstr., 1910, ii, 285) into three classes, for example, phase isomerism, component isomerism, and dynamic isomerism, is criticised as quite unnecessary, dynamic isomerism, being regarded as only a special case of phase isomerism. Two substances of the same molecular composition are either identically constructed (polymorphic) or of different structure (isomeric).

Isomerisation, denoting the conversion of a substance *A* into another *B* of the same composition, is either spontaneous and complete, or when a mixture of *A* and *B* is formed, whichever was originally taken, it is reciprocal.

Homochromoisomerism (Hantzsch, Abstr., 1910, i, 474), in which the isomerides differ in m. p. and solubility, but are identical chemically and optically, is considered to be completely explained by the ordinary

conceptions of polymorphism. The case of picrylphenylmethylamine studied by Hantzsch (*loc. cit.*), which exists in two modifications, m. p. 108—110° and m. p. 128—129° respectively, has been further investigated.

The amine, m. p. 128°, crystallised from benzene, yields the amine, m. p. 108°, but contrary to Hantzsch, the reverse change could not be effected. The two amines are converted into one another by fusion and innoculation. The amine, m. p. 108°, when heated at 100° or at a temperature above 108°, is converted into the amine, m. p. 128°. The reverse change takes place when the amine, m. p. 128°, is heated for a short time above this temperature and quickly cooled. E. F. A.

Chlorination of α-Naphthol. ARNOLD REISSERT (*Ber.*, 1911, **44**, 865—869).—4-Chloro-α-naphthol, which cannot be obtained by the direct chlorination of α-naphthol, is readily produced by treating a methyl-alcoholic solution of 1-hydroxy-2-naphthoic acid with chlorine (1 mol.) at 30—40°, and heating the resulting 4-*chloro*-1-*hydroxy*-2-*naphthoic acid*, m. p. 234°, with aniline and naphthalene at 170—180°, whereby carbon dioxide is eliminated.

4-Chloro-1-hydroxy-2-naphthoic acid reacts with boiling aqueous sodium nitrite to form a *compound*, $C_{10}H_6O_2NCl,C_{11}H_7O_3Cl$, of chlorohydroxynaphthoic acid and 4-chloro-β-naphthaquinoneoxime. 4-*Chloro*-β-*naphthaquinoneoxime*, $C_6H_4<\begin{matrix}CO-C:NOH\\ CCl:CH\end{matrix}$, m. p. 157°, pale yellow needles, is obtained by treating an alcoholic solution of 4-chloro-1-naphthol at 0° with concentrated hydrochloric acid and sodium nitrite; it is purified by means of its sparingly soluble, red *sodium* salt.

C. S.

4-Nitroresorcinol. HUGO KAUFFMANN and W. KUGEL (*Ber.*, 1911, **44**, 753—756).—The nitro-derivatives of dihydric phenols are most readily prepared by nitrating their monobenzoates. Resorcinol monobenzoate yields two isomeric nitro-derivatives, but both yield 4-nitroresorcinol (Weselsky and Benedikt, Abstr., 1881, 727) on hydrolysis.

Resorcinol monobenzoate crystallises from benzene, and has m. p. 133°; it is best nitrated by dissolving in ten times its weight of glacial acetic acid, cooling to 20—22°, adding nitric acid (D 1·2), and allowing the temperature to rise to 36—38° and then diluting with its own volume of water. It is essential to work under specific conditions, as otherwise resinous masses or the original compound are obtained. The 1 : 3 : 4-*derivative* is sparingly soluble in chloroform, and crystallises from 50% alcohol in colourless needles, m. p. 189°; it dissolves in dilute sodium carbonate, yielding a yellow solution; the isomeric 1 : 3 : 6-*derivative* is readily soluble in chloroform, crystallises from glacial acetic acid in yellow needles, m. p. 124°, and with sodium carbonate yields a sparingly soluble, orange-coloured sodium derivative. 4-Nitroresorcinol has m. p. 122° (not 115°), and its dimethyl ether, m. p. 75°. J. J. S.

New Series of Aromatic Sulphur Compounds. THEODOR ZINCKE (*Ber.*, 1911, **44**, 769—771).—Compounds of the type

C_6H_5·SCl can be obtained by the action of chlorine on the benzyl ethers of aromatic mercaptans. The reaction is entirely different from that between the corresponding methyl ethers and chlorine (Abstr., 1909, i, 644; 1910, i, 314; this vol., i, 40). The same type of compound is also formed by the action of chlorine on the mercaptans or their disulphides.

4 : 4′-*Dichlorothioldiphenyl*, SCl·C_6H_4·C_6H_4·SCl, crystallises from carbon tetrachloride in yellow prisms, m. p. 115°, and decomposes at 140°. 4 : 6-*Dichloro*-1 : 3-*dichlorothiolbenzene*, $C_6H_2Cl_2(SCl)_2$, obtained by the action of chlorine on a chloroform solution of 1 : 3-dithiolbenzene, crystallises from hexane in yellow needles, m. p. 103°. o-*Nitrochlorothiolbenzene*, NO_2·C_6H_4·SCl, prepared by the action of chlorine on *o*-*o*′-dinitrodiphenyl disulphide suspended in carbon tetrachloride, crystallises in long, yellow needles, m. p. 75°. The chlorine derivatives are transformed into disulphides when boiled with alcohol or treated with aqueous alkali solutions. They also react with acetone, the chlorine of the ·SCl group being replaced by ·CH_2·CO·CH_3.

The corresponding bromine derivatives are not so easy to prepare, and the compound described by Otto (*Annalen*, 1868, **145**, 329) as C_6H_5·SBr is shown to be the disulphide $(C_6H_4Br)_2S_2$. J. J. S.

Action of Ethyl Alcohol on Toluene-*p*-diazonium Hydrochloride and of Sulphuric Acid on *p*-Tolyl Ethyl Ether. PERCIVAL RUDOLPH ROBERTS and GELLERT ALLEMAN (*J. Amer. Chem. Soc.*, 1911, **33**, 391—396).—In an earlier paper (Alleman, Abstr., 1904, i, 202), it was shown that *p*-tolyl methyl ether can be readily obtained by the action of methyl alcohol on *p*-toluenediazonium sulphate, and that when treated with sulphuric acid, it is converted into *p*-methoxytoluene-*m*-sulphonic acid. Attempts to prepare *p*-tolyl ethyl ether in a similar manner did not yield good results, but a method is now described by which it can be obtained in a yield of 35% of the theoretical.

The diazonium compound is prepared from *p*-toluidine hydrochloride instead of the sulphate, as the former is more soluble in ethyl alcohol. The ethyl ether is thus obtained as an oil, b. p. 187—191°, $[n]_D^{15}$ 1·51069, which is identical with the compound described by Engelhardt and Latschinow (*Zeitsch. Chem.*, 1869, 619).

p-Tolyl ethyl ether reacts with concentrated sulphuric acid at the ordinary temperature with formation of p-*ethoxy*-m-*toluenesulphonic acid*, OEt·C_6H_3Me·SO_3H, m. p. 92—92·5°, which forms colourless, transparent crystals; its *barium*, *potassium*, *sodium*, *calcium*, *zinc*, *nickel*, *copper*, and *lead* salts are described. E. G.

Hexahydrohippuric Acid. MARCEL GODCHOT (*Bull. Soc. chim.*, 1911, [iv], **9**, 261—264).—The preparation of hexahydrohippuric acid and of a number of its derivatives is described.

*cyclo*Hexanecarboxyl chloride, b. p. 179—180°/760 or 100°/40 mm. (compare Meyer and Scharvin, Abstr., 1897, i, 612), reacts with glycine to form *hexahydrohippuric acid*, C_6H_{11}·CO·NH·CH_2·CO_2H, m. p. 152°, which crystallises in colourless needles, is sparingly soluble in water, alcohol, or ether, but much more so on warming, reddens litmus,

and gives a characteristic *copper* salt. The *methyl* ester, m. p. 100—101°, and the *ethyl* ester, m. p. 75—76°, both crystallise in needles. The *amide*, m. p. 195—196°, obtained from the ethyl ester by the action of ammonia solution, separates from warm water in small crystals. On distillation at atmospheric pressure with zinc chloride, the acid furnishes *cyclo*hexanecarboxylonitrile, b. p. 184—185°/760 mm. (compare Demjanoff, Abstr., 1904, i, 410).

T. A. H.

Ethyl Polycinnamate. CARL LIEBERMANN and MILAN ZSUFFA (*Ber.*, 1911, **44**, 841—849).—In connexion with attempts to accelerate the rate of spontaneous polymerisation of the esters of cinnamic acid, the authors have prepared methyl, *iso*amyl, benzyl, allyl, and *octyl* cinnamates. The last is obtained by boiling equal molecular quantities of cinnamyl chloride and octan-β-ol in three times the weight of benzene to which pyridine (1·5 mol.) is added, and has b. p. 240°/60 mm. However, only the ethyl and the *iso*amyl esters polymerise to an extent suitable for practical purposes. After many trials, the following process is adopted, by which polymerised ethyl cinnamate is obtained in comparatively large quantities. Ethyl cinnamate, about 100—200 grams, is distilled under ordinary pressure, and the distillate is inoculated with the polymeride and heated for some days at 80—85°. The liquid becomes gelatinous, and contains about 6% of the isomeride; the latter is precipitated by ether and removed, whilst the unchanged ester, after being recovered, is redistilled and again treated as above. In this way about 20% of the ethyl cinnamate can be converted into its polymeride.

The esters of polycinnamic acid are white, infusible, friable substances, which are almost insoluble in all solvents, and are odourless even after very long keeping. When heated, ethyl polycinnamate at first blackens, but as depolymerisation occurs, the distillation proceeds smoothly, and almost the whole of the polymeride is obtained as ethyl cinnamate.

Ethyl polycinnamate resists hydrolysis even by prolonged boiling with concentrated aqueous or alcoholic potassium hydroxide, acetic and 50% sulphuric acids, or *p*-toluidine. The hydrolysis can be effected, although not completely, by the following two methods. The polymeride is covered with a little acetic anhydride, and heated for ten to twelve hours at 160° with hydriodic acid, D 1·96, whereby ethyl iodide is produced; the product is washed with very dilute sulphurous acid and with very dilute alkali, is dissolved in boiling water, and the polycinnamic acid is precipitated in gelatinous flocks by hydrochloric acid. In the second method the ethyl polycinnamate is intimately mixed with aluminium chloride and antimony chloride, and is heated for some hours on the water-bath, and finally at 130—140° for two to three hours; the product is digested with 25% hydrochloric acid, washed with 35% tartaric acid and with water, and is finally dissolved in hot alkali and precipitated as above.

Polycinnamic acid (?), m. p. above 260°, is stable to alkaline potassium permanganate. Its analysis points to the composition $C_{27}H_{22}O_5$, that is, 3 mols. of cinnamic acid minus 1 mol. of water, whilst

titration with $N/10$-sodium hydroxide and phenolphthalein shows that it is dibasic.

The authors make the following deductions from the preceding results. Ethyl polycinnamate, which is undoubtedly a true polymeride of ethyl cinnamate, probably has the constitution:

$$\begin{array}{l} CH(CO_2Et)\cdot CHPh\cdot CH\cdot CO_2Et \\ CHPh \text{——} CHPh \text{——} CH\cdot CO_2Et \end{array}.$$

The polycinnamic acid (?) obtained by its hydrolysis would then be $\begin{array}{l} CH(CO_2H)\cdot CHPh\cdot CH\cdot CO \\ CHPh \text{——} CHPh \text{——} CH\cdot CO \end{array}\!\!>\!O$. Since, however, an acid of this constitution would be either mono- or tri-basic, and, moreover, since in the ester the carbethoxy-group between the two CHPh groups very probably is unattacked during hydrolysis, polycinnamic acid (?) might have the constitution: $\begin{array}{l} CH(CO_2Et)\cdot CHPh\cdot CH\cdot CO \\ CHPh \text{——} CHPh \text{——} CH\cdot CO \end{array}\!\!>\!O$, a formula which does not agree quite as well as the former with the analytical results, but has the advantage of representing polycinnamic acid (?) as the anhydride of a dibasic acid. C. S.

The Utilisation of Carbalkyloxy-derivatives for the Estimation of Hydroxyl Groups. K. C. R. DANIEL and MAXIMILIAN NIERENSTEIN (*Ber.*, 1911, **44**, 701—704).—The method of estimation consists in hydrolysing the carbalkyloxy-derivative by heating it with 50% pyridine at 115—120°, and weighing the carbon dioxide evolved, the gas being freed from pyridine vapour by passing through a tube containing a mixture of oxalic acid and calcium chloride. A sketch of the apparatus employed is given.

The following new compounds, prepared according to Fischer's method, are described:

m-*Ethylcarbonatobenzoic acid*, $CO_2Et\cdot O\cdot C_6H_4\cdot CO_2H$, crystallises in needles, m. p. 98°.

p-*Nitrophenyl ethyl carbonate*, $CO_2Et\cdot O\cdot C_6H_4\cdot NO_2$, forms needles, m. p. 67—68°.

4-*Ethylcarbonato*-m-*nitrobenzoic acid*, $CO_2Et\cdot O\cdot C_6H_3(NO_2)\cdot CO_2H$, crystallises in pale yellow cubes, m. p. 176—177°. F. B.

Carbamides Derived from α-Amino-p-hydroxyphenylacetic Acid and its Methyl Ether. JULES ALOY and CHARLES RABAUT (*Bull. Soc. chim.*, 1911, [iv], 9, 253—255. Compare Abstr., 1910, i, 558).—Phenylcarbamide and carbamide derivatives of these two acids have been prepared, similar to those obtained by Hugounenq and Morel from tyrosine and leucine (Abstr., 1906, i, 85).

The sodium salt of α-amino-p-hydroxyphenylacetic acid reacts with phenylcarbimide to form diphenylcarbamide and a mixed *carbamide*, $NHPh\cdot CO\cdot NH\cdot CH(CO_2H)\cdot C_6H_4\cdot OH$, m. p. 193°, which is sparingly soluble in water, readily so in alcohol, and insoluble in ether or chloroform. α-Amino-p-methoxyphenylacetic acid gives a similar derivative, m. p. 198° (approx.). When the sodium salts of the two amino-acids are treated with carbonyl chloride, they give rise to the corresponding symmetrical *derivatives* of carbamide, $CO[NH\cdot CH(CO_2H)\cdot C_6H_4\cdot OH]_2$

and $CO[NH\cdot CH(CO_2H)\cdot C_6H_4\cdot OMe]_2$ respectively. Both are amorphous, pale yellow powders; the second has m. p. 150° (decomp.).

T. A. H.

Preparation of 3 : 5-Di-iodotyrosine from Iodoproteins. II. The Obtaining of the Same from Iodoglidin. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, **71**, 200—203. Compare this vol., i, 203).—It has been shown previously that 3 : 5-di-iodotyrosine is obtained from the commercial iodised protein called iodo-albacid. The same product is also obtained from iodo-glidin, an iodised protein containing 9·2% of iodine in organic combination, prepared from wheat.

W. D. H.

Reduction of the Anhydroxime of *o*-Benzoylbenzoic Acid. ROBERT EVSTAFIEFF ROSE (*J. Amer. Chem. Soc.*, 1911, **33**, 388—391).—The oxime of *o*-benzoylbenzoic acid, like those of other compounds containing a carboxyl group in the ortho-position to the carbonyl group, cannot exist in the free state, but, when liberated from its alkali salts, is instantly converted into the anhydride, $C_6H_4<\begin{matrix}CPh:N\\ CO—O\end{matrix}$ (Thorp, Abstr., 1893, i, 446, 589).

This anhydro-compound has m. p. 161—163°. When reduced with zinc dust and glacial acetic acid, it yields a stable, crystalline *lactam*, $C_6H_4<\begin{matrix}CHPh\\ CO\end{matrix}>NH$, m. p. 218—220°, which furnishes an *acetyl* derivative, m. p. 153—155°. If the lactam is heated with concentrated sulphuric acid for four hours at 160—170°, a sulphonic acid is produced, which yields a *barium* salt, $(C_{14}H_{10}O_4NS)_2Ba,2H_2O$. On distilling the lactam with zinc dust, a strongly fluorescent, oily product was obtained, which contained carbazole; the fluorescent substance was not present in sufficient quantity to enable it to be identified.

E. G.

Benzoylphenylacetamide. TREAT B. JOHNSON and LEWIS H. CHERNOFF (*J. Amer. Chem. Soc.*, 1911, **33**, 517—520).—By the action of benzoyl chloride on phenyl-phenylethenylamidine, Wheeler, Johnson, and McFarland (Abstr., 1903, i, 859) obtained benzoylphenylacetamide, m. p. 129—130°. Benzoylphenylacetamide was previously described by Colby and Dodge (Abstr., 1891, 409), who obtained it by heating benzonitrile with phenylacetic acid, or phenylacetonitrile with benzoic acid, and found its m. p. to be 171°. On repeating Colby and Dodge's experiments, it has been found that the product obtained is not benzoylphenylacetamide, but a mixture of dibenzamide and diphenyldiacetamide.

Benzoylphenylacetamide, m. p. 129—130°, can be prepared in nearly theoretical yield by the action of benzoylcarbimide on phenylacetic acid at the ordinary temperature, and the product thus obtained is identical with that described by Wheeler, Johnson, and McFarland (*loc. cit.*).

When benzoylthiocarbimide is heated with phenylacetic acid at 104—110°, diphenyldiacetamide is produced.

Benzoylcarbimide reacts readily with β-phenylpropionic acid, with formation of β-phenylpropionylbenzamide, m. p. 104—105° (Colby and Dodge, *loc. cit.*). E. G.

Fulgides. HANS STOBBE (*Annalen*, 1911, **380**, 1—129. Compare Abstr., 1904, i, 588, 589, 672, 673; 1905, i, 857; 1906, i, 22, 91, 92, 101, 183, 278, 279, 361, 960; 1908, ii, 339).—I. *Relation between Colour and Constitution of Fulgides.*—The absorption spectra of chloroform solutions of the following compounds have been determined, using a Nernst lamp placed 30 cm. from a 10 mm. layer of a $1/32N$-solution and giving an exposure of three minutes: α-phenyl-, α-*p*-tolyl-, α-cumyl-, α-*o*-nitrophenyl-, α-*m*-nitrophenyl-, α-*o*-anisyl-, α-anisyl-, α-veratryl-, and α-piperonyl-δδ-dimethyl-fulgide; α-phenyl-αδδ-triphenylfulgide; αδ-diphenyl-, αδ-diphenyl-δ-methyl-, αα-diphenyl-δδ-dimethyl-, α-anisyl-δ-phenyl-, α-piperonyl-δ-phenyl-, αδ-dicumyl-, αδ-dianisyl-, αδ-diveratryl-, αδ-dipiperonyl-, and αδδ-triphenyl-fulgide; α-*p*-tolyl-, α-cumyl-, α-*p*-chlorophenyl-, α-*o*-nitrophenyl-, α-*m*-nitrophenyl-, α-*p*-nitrophenyl-, α-*o*-anisyl-, α-anisyl-, α-veratryl-, and α-piperonyl-δδ-diphenylfulgide; ααδδ-tetraphenylfulgide. Photographs of the absorption spectra and the value of the absorption limit in the violet end of the spectrum are given. The absorption depends on three factors: (*a*) the unsaturated (quinonoid) structure of the fulgide ring; (*b*) the number of aryl groups present, and (*c*) the nature and position of the auxochromes present in the aryl groups. An increase in the number of aryl groups increases the absorption in the violet end; the presence of alkyl, nitro-, and methoxy-groups also tends to increase the absorption, more especially when they are in the para-position. When present in the meta-position the effect is only slight. By suitably varying *b* and *c*, it is possible to obtain fulgides with any desired nuance.

The colour tone can also be altered by the introduction of a large number of olefine linkings in the fulgide molecule; for example, by introducing styryl in place of phenyl groups. Thus α-phenyl-δδ-dimethylfulgide is sulphur-yellow, whereas the corresponding α-styryl compound is golden-yellow; the αδ-diphenyl compound is lemon-yellow, and the α-styryl-δ-phenyl derivative orange; the αδδ-triphenyl compound, orange-red, and the α-styryl-δδ-diphenylfulgide, ruby-red (compare also Fittig and Batt, Abstr., 1904, i, 744). Naphthylfulgides have deeper colours than the corresponding phenyl derivatives, and, similarly, the α-diphenylenefulgides have deeper colours than the corresponding α-diphenyl compounds.

II. *Thermochromic Phenomena* (compare Stobbe and Vigier, Abstr., 1904, i, 672; Hantzsch, 1906, i, 353; Senier and Shepheard, Trans., 1909, **95**, 1943).—The colours of the various fulgides have been examined at the ordinary temperature, at −80° to −180°, and at higher temperatures, namely, 70° to 140°. A rise of temperature produces a change in colour, indicated by the order: greenish-yellow, yellow, orange, brown, red, purple, violet, blue, and a fall in temperature a change in the opposite direction. For any given compound each temperature has a corresponding colour tone, and the colour of the compound always returns to the tone corresponding with the

temperature at which it is kept. The changes which the pale yellow monoarylfulgides undergo are not so marked as those characteristic of the deeper coloured polyaryl compounds, that is, the latter compounds are more sensitive to thermochromic influences. The solid fulgides are also phototropic (Abstr., 1908, ii, 339), and the deepening in colour produced by exposure to light can be removed by a slight increase in temperature, and by a further rise of temperature a second deepening of the colour is produced. The conclusion is drawn that all compounds which are both phototropic and thermochromic undergo two distinct reversible changes which are characterised by colour alterations.

III. *Monoarylfulgenic Acids and their Fulgides.*—By the condensation of an aromatic aldehyde with ethyl tetraconate in the presence of sodium ethoxide a single fulgenic acid is usually obtained.

Cuminaldehyde, however, yields two stereoisomeric α-cumyl-δδ-dimethylfulgenic acids (Abstr., 1906, i, 22), together with an isomeric lactonic acid, and *p*-chlorobenzaldehyde yields mainly a lactonic acid. All the monoarylfulgenic acids are oxidised by permanganate to oxalic acid, acetone, and the aldehyde from which they were synthesised. Acetyl chloride transforms the acids into their yellow anhydrides, each acid yielding as a rule a corresponding fulgide. The two stereoisomeric cuminyldimethylfulgenic acids yield stereoisomeric fulgides; the *allo*-fulgide has a somewhat broader absorption band ($\lambda = 412\mu\mu$) than the isomeride ($\lambda = 407\mu\mu$). α-Phenyl-δδ-dimethylfulgenic acid yields two stereoisomeric fulgides, the one colourless and the other yellow; both have the same m. p. and the same chemical properties, but the colours of their solutions are different.

[With ALFRED LENZNER].—*α-Veratryl-δδ-dimethylfulgenic acid*,

$$CMe_2:C(CO_2H)\cdot C(CO_2H):CH\cdot C_6H_3(OMe)_2,$$

crystallises from water in nodular masses, m. p. 194·5° (decomp.) after sintering at a lower temperature; the corresponding *fulgide*, $C_{16}H_{16}O_5$, crystallises from light petroleum in yellow prisms, resembling sodium picrate, and has m. p. 127·5°. *α-Piperonyl-δδ-dimethylfulgenic acid*, $CMe_2:C(CO_2H)\cdot C(CO_2H):CH\cdot C_6H_3:O_2:CH_2$, separates as colourless crystals from ethyl acetate, and has m. p. 203—204°; when reduced with sodium amalgam in alkaline solution, it yields *ε-piperonyl-β-methyl-Δ^β-pentene-γδ-dicarboxylic acid*,

$$CH_2O_2:C_6H_3\cdot CH_2\cdot CH(CO_2H)\cdot C(CO_2H):CMe_2,$$

which crystallises from 10% acetic acid, and has m. p. 135° (decomp.). *α-Piperonyl-δδ-dimethylfulgide*, $C_{15}H_{12}O_5$, forms yellow crystals, m. p. 145—146°. A by-product, formed in the preparation of the fulgenic acid, crystallises from chloroform in yellow needles, m. p. 191°, and is probably *dimethylenedioxystilbene*, $C_2H_2(C_6H_3:O_2:CH_2)_2$; it yields a *dibromide*, m. p. 173°.

[With EMIL WAHL.]—The *lactonic acid*, obtained by condensing *p*-chlorobenzaldehyde with ethyl tetraconate and sodium ethoxide in the presence of anhydrous ether, is either *γ*-p-*chlorophenyl-α*-iso*propylene-paraconic acid*, $C_6H_4Cl\cdot CH<\begin{matrix}CH(CO_2H)\\ O\text{———}CO\end{matrix}>C:CMe_2$, or *α*-p-*chloro-benzylidene-γγ-dimethylparaconic acid*,

$$C_6H_4Cl\cdot CH:C<\begin{matrix}CH(CO_2H)\\ CO\text{———}O\end{matrix}>CMe_2.$$

It crystallises from ether, has m. p. 220°, and when warmed with acetyl chloride the greater portion is recovered unaltered, but a small amount of *a*-p-*chlorophenyl-δδ-dimethylfulgide* is obtained as pale yellow crystals, m. p. 133°, and $\lambda = 415\mu\mu$.

IV. *The Stereoisomeric Ethyl Phenylmethylitaconates and their Colour Reactions* (compare Abstr., 1904, i, 503).—The *cis*-acid with concentrated sulphuric acid yields a yellow methylindoneacetic acid, the solution of which in sulphuric acid has a deep violet coloration. The normal and acid esters of the *cis*-acid give the same coloration. The *trans*-acid and its esters, on the other hand, dissolve in concentrated sulphuric acid, yielding yellow solutions, and this difference in coloration affords a basis for determining whether in such compounds the phenyl and carboxyl groups are in the *cis*- or *trans*-positions with respect to one another.

[With FERDINAND GADEMANN.]—Ethyl phenylmethyl*iso*itaconate (Abstr., 1899, i, 902) is best prepared from the silver salt of the ethyl hydrogen ester, and has b. p. 305—307°.

[With ROBERT ROSE.]—*Ethyl phenylmethylitaconate*, $C_{16}H_{20}O_4$, when prepared by the hydrogen chloride or sulphuric acid catalytic method contains a certain amount of anhydride; it is best prepared from the silver salt, and is a pale yellow oil, b. p. 314—316°. The corresponding *methyl* ester, $C_{14}H_{16}O_4$, has b. p. 182·5—183°/20 mm.

V. *The Stereoisomeric Phenyltrimethylfulgenic Acids and their Fulgides.*—[With FERDINAND GADEMANN.]—*a*-Phenyl-*a*δδ-trimethylfulgenic acid exists in two stereoisomeric modifications:

$$\begin{matrix}CH_3\\C_6H_5\end{matrix}\!\!>C{:}C<\!\!\begin{matrix}C(CO_2H){:}CMe_2\\CO_2H\end{matrix}$$

and, *allo*, $\begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>C{:}C<\!\!\begin{matrix}C(CO_2H){:}CMe_2\\CO_2H\end{matrix}$. The fulgenic acid alone is obtained by the condensation of acetone with ethyl phenylmethyl*iso*itaconate, whereas a mixture of the two stereoisomeric fulgenic acids and phenylmethylitaconic acid is obtained when acetone is condensed with ethyl phenylmethylitaconate and sodium ethoxide. Acetophenone and ethyl dimethylitaconate condense in the presence of sodium ethoxide, yielding a mixture of the two fulgenic acids.

*a-Phenyl-a*δδ-*trimethylfulgenic acid* crystallises from water in small, colourless needles, m. p. 221—223° (decomp.), and gives an intense violet coloration with sulphuric acid. With acetyl chloride, it yields *a-phenyl-a*δδ-*trimethylfulgide*, $C_{15}H_{24}O_3$, which forms colourless crystals with a yellowish-green reflex, and has m. p. 112—113°. *a-Phenyl-a*δδ-*trimethyl*allo*fulgenic acid* is identical with the compound described by Stobbe and Rose (Abstr., 1905, i, 857) as δ-phenyl-*aa*δ-trimethylfulgenic acid, and has m. p. 208—210° (decomp.). Details for its preparation are given. The corresponding *allo*fulgide is identical with the compound described as δ-phenyl-*aa*δ-trimethylfulgide. It forms lemon-yellow needles, m. p. 132—133°, and is the stable form, as it can be obtained from its stereoisomeride (1) by exposing a chloroform solution containing a little iodine to sunlight; (2) by prolonged boiling of its xylene solution; (3) by heating with naphthalene for twelve hours at 190°. An *N*/32-chloroform solution of the *allo*fulgide has a rather broader absorption band ($\lambda = 405\mu\mu$) than a similar solu-

tion of its isomeride ($\lambda = 402\mu\mu$). As in the case of many other pairs of stereoisomeric fulgides, the more stable and less fusible compound is the more deeply coloured.

VI. *Diarylated Fulgenic Acids and their Fulgides.*—Good yields of $\alpha\delta$-diarylated fulgenic acids can be obtained by condensing the ester of a γ-arylated itaconic acid with an aromatic aldehyde in the presence of an alcoholic solution of sodium ethoxide, or of the solid ethoxide and anhydrous ether. Hydroxy-acids of the type

$$R\cdot CH(OH)\cdot CH(CO_2H)\cdot C(CO_2H):CHR',$$

are sometimes formed. Although the fulgenic acid can exist theoretically in three ($R = R'$) or four stereoisomeric forms, the acids obtained are usually homogeneous. The same acids can also be synthesised by condensing ethyl succinate with an excess of an aromatic aldehyde in the presence of sodium ethoxide (compare Abstr., 1906, i, 102). This method is less expensive, but is complicated by the formation of various by-products, for example, γ-arylated paraconic and itaconic acids, lactonic acids isomeric with the fulgenic acids, and aromatic monobasic acids and alcohols formed by the action of the alkali on the aldehyde. The various aldehydes react differently with ethyl succinate. Benzaldehyde, p-*iso*propylbenzaldehyde, anisaldehyde, and piperonaldehyde give 40% yields of the corresponding diarylated fulgenic acids. Low temperatures ($-10°$ to $-17°$) favour the formation of these acids, whereas higher temperatures tend to form resins or substituted itaconic acids. Veratraldehyde gives but a poor yield of diveratrylfulgenic acid, and nitrobenzaldehydes yield resins. Practically all the acids can be reduced to the corresponding diarylated butanedicarboxylic acids, which yield colourless anhydrides. The lactonic acids formed during the condensation of aromatic aldehydes with itaconic esters can be transformed into the isomeric fulgenic acids by boiling with sodium ethoxide solution, and it is probable that in all cases lactonic acids are intermediate products in the formation of fulminic acids.

[With ROBERT ROSE.]—*Ethyl hydrogen $\alpha\delta$-diphenyl-δ-methylfulgenate*, $C_{21}H_{20}O_4$, prepared by allowing a solution of benzaldehyde, γ-phenyl-γ-methylitaconic ester, and sodium ethoxide in ethyl alcohol to remain for four hours at the ordinary temperature, forms colourless, rhombic crystals, m. p. 172—173°. The corresponding *acid* crystallises from 50% acetic acid in colourless prisms, m. p. 212—214° (decomp.) after softening at 180°, and appears to be a mixture of the acid with a monohydrate. *$\alpha\delta$-Diphenyl-δ-methylfulgide*, $C_{19}H_{14}O_3$, crystallises from ether in glistening, lemon-yellow, hexagonal prisms, m. p. 148°.

[With GEORG POSNJAK.]—$\alpha\alpha$-Diphenyl-$\delta\delta$-dimethylfulgenic acid (Abstr., 1905, i, 857) can also be prepared by condensing acetone with diphenylitaconic ester and sodium ethoxide, and its solution in concentrated sulphuric acid has a deep green colour, similar to that of diphenylitaconic acid in sulphuric acid, and in both cases an indone derivative is formed.

[With KARL KAUTZSCH and TH. BADENHAUSEN.]—*δ-Phenyl-α-piperonylfulgenic acid*, $CH_2O_2:C_6H_3\cdot CH:C(CO_2H)\cdot C(CO_2H):CHPh$, is obtained mixed with the corresponding hydroxy-acid by condensing piperonaldehyde and phenylitaconic ester. The mixture forms pale yellow, nodular masses from ether, m. p. 203—206° (decomp.), and the corre-

sponding *fulgide*, $C_{19}H_{12}O_5$, crystallises from a mixture of ether and chloroform in pale orange-coloured prisms, m. p. 169—170°.

VII. *aδ-Dicumylfulgenic Acids, Cumylitaconic Acid, and Cumylparaconic Acid.*—[With RICHARD HÄRTEL.]—A mixture of the four acids is obtained by condensing cuminaldehyde with ethyl succinate in the presence of pure sodium ethoxide and anhydrous ether.

The yellow *aδ-dicumylfulgenic acid*,

$$C_6H_4Pr^{\beta}\cdot CH:C(CO_2H)\cdot C(CO_2H):CH\cdot C_6H_4Pr^{\beta},$$

separates from light petroleum in sulphur-yellow crystals, or from chloroform in whitish-grey crystals containing chloroform of crystallisation. It has m. p. 220° (decomp.).

The corresponding *fulgide*, $C_{24}H_{24}O_3$, separates from light petroleum in orange-red, triangular plates or long needles, m. p. 112—113°. The colourless *aδ-dicumyl*iso*fulgenic acid* is found as its methyl hydrogen salt in the light petroleum mother liquors of the yellow acid. It crystallises from chloroform with solvent of crystallisation, and has m. p. 225° (decomp.). The corresponding *fulgide* is not so readily prepared as the isomeride, and crystallises in lemon-yellow plates or needles, m. p. 112—113°. Both the fulgenic acids, on reduction with sodium amalgam in the presence of carbon dioxide, yield *aδ-dicumylbutane-βγ-dicarboxylic acid*, $C_6H_4Pr^{\beta}\cdot CH_2\cdot CH(CO_2H)\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4Pr^{\beta}$, which crystallises from benzene, and has m. p. 220°. The colourless *iso*-acid is not so readily oxidised by permanganate as the yellow acid, and both fulgides react with bromine, yielding amorphous products.

Cumylparaconic acid, $C_6H_4Pr^{\beta}\cdot CH{<}\begin{matrix}CH(CO_2H)\cdot CH_2\\ O\text{———————}CO\end{matrix}$, is isolated as an oil, which solidifies after several months, crystallises from water or chloroform, and has m. p. 158°.

Cumylitaconic acid, $C_6H_4Pr^{\beta}\cdot CH:C(CO_2H)\cdot CH_2\cdot CO_2H$, crystallises from a mixture of ether and light petroleum, has m. p. 200°, and gives a bluish-green coloration with concentrated sulphuric acid. The *anhydride*, $C_{14}H_{14}O_3$, crystallises from light petroleum in colourless, glistening prisms, m. p. 138°. Both paraconic and itaconic acids yield *cumyl*iso*paraconic acid* when boiled with 50% sulphuric acid. This acid crystallises from water in colourless needles, m. p. 131°, and, when moistened with concentrated sulphuric acid, gives no coloration for the first moment, but gradually develops a yellow colour.

VIII. *aδ-Dianisylfulgenic Acid and an Isomeric Lactonic Acid.*—[With ERICH BENARY.]—*aδ-Dianisylfulgenic acid*,

$$OMe\cdot C_6H_4\cdot CH:C(CO_2H)\cdot C(CO_2H):CH\cdot C_6H_4\cdot OMe,$$

and the isomeric lactonic acid, *a-anisylidene-γ-*p-*methoxyphenylparaconic acid*, $OMe\cdot C_6H_4\cdot CH{<}\begin{matrix}CH(CO_2H)\\ O\text{————}CO\end{matrix}{>}C:CH\cdot C_6H_4\cdot OMe$, are obtained by the condensation of anisaldehyde with ethyl succinate in the presence of sodium ethoxide, and can be separated by means of benzene, in which the fulgenic acid is insoluble. This acid crystallises from glacial acetic acid or alcohol in lemon-yellow prisms, m. p. 242—243° (decomp.), after softening at 220°. The corresponding *fulgide*,

$$C_{20}H_{16}O_5,$$

crystallises from carbon disulphide in chrome-yellow needles, m. p

170—171°. The lactonic acid crystallises from benzene, is colourless, and has m. p. 108—109°. It is transformed into the fulgenic acid when boiled for twelve hours with potassium ethoxide solution.

IX. *αδ-Diveratrylfulgenic Acid.*—[With KARL LEUNER.]—αδ-Diveratrylfulgenic acid and γ-veratrylitaconic acid are formed by the condensation of veratraldehyde with ethyl succinate, and the yield of the former is greater when an excess of aldehyde is used, but, as much resin is also formed under these conditions, the purification of the acids is rendered more tedious. A modification of Tiemann's method (this Journ., 1876, i, 76) for the preparation of veratraldehyde from vanillin is described. *Diveratrylfulgenic acid*,

$$C_6H_3(OMe)_2\cdot CH\dot{:}C(CO_2H)\cdot C(CO_2H)\dot{:}CH\cdot C_6H_3(OMe)_2,$$

is insoluble in chloroform, crystallises from dilute alcohol, and has m. p. 220° (decomp.). The *fulgide*, $C_{22}H_{20}O_7$, crystallises from benzene in brilliant red, monoclinic plates, or large, double pyramids, m. p. 172—173°. *γ-Veratrylitaconic acid*,

$$C_6H_3(OMe)_2\cdot CH\dot{:}C(CO_2H)\cdot CH_2\cdot CO_2H,$$

crystallises from water or chloroform in slender, colourless needles, m. p. 175°, and yields an insoluble *barium* salt. The *anhydride*, $C_{13}H_{12}O_5$, crystallises from benzene in orange-red needles containing benzene, or in crusts of yellow prisms free from benzene. The hydrocarbon is removed at 80°, and then both forms melt at 167°.

X. *αδ-Piperonylfulgenic Acid and an Isomeric Lactonic Acid.*—[With WALTER VIEWEG, RICHARD ECKERT, and GUSTAV REDDELIEN.]—The lactonic acid, *α-piperonylidene-γ-methylenedioxyphenylparaconic acid*, $CH_2O_2\dot{:}C_6H_3\cdot CH<\begin{matrix}CH(CO_2H)\\O\text{———}CO\end{matrix}>C\dot{:}CH\cdot C_6H_3\dot{:}O_2CH_2$, is the chief product formed when ethyl succinate and piperonaldehyde are left in contact with dry ether and sodium ethoxide for a short time at low temperatures. The product formed is the sodium salt of the corresponding hydroxy-acid, but when acidified this yields the colourless lactonic acid, which crystallises from acetic acid and has m. p. 182°. The acid is not affected by acetyl chloride, but with acetic anhydride yields a compound, $C_{24}H_{16}O_9$, with m. p. 265°. *αδ-Dipiperonylfulgenic acid*,

$$CH_2\dot{:}O_2\dot{:}C_6H_3\cdot CH\dot{:}C(CO_2H)\cdot C(CO_2H)\dot{:}CH\cdot C_6H_3\dot{:}O_2\dot{:}CH_2,$$

is formed when the reaction mixture is kept for eight days at low temperatures, or when the lactonic acid is boiled for twelve hours with potassium ethoxide solution. It crystallises from glacial acetic acid in yellow prisms containing 2 molecules of acetic acid, which it loses at the ordinary temperature. The acid has then an orange-yellow colour, and m. p. 210° (decomp.). The *potassium* salt, $C_{20}H_{12}O_8K_2$, crystallises from 80% ethyl alcohol in yellow needles; the *ethyl* ester, $C_{24}H_{22}O_8$, in greenish-yellow, felted needles, m. p. 133°, and the *fulgide*, $C_{20}H_{12}O_7$, separates from chloroform in orange-coloured crystals, m. p. 210°. When reduced with sodium amalgam in the presence of carbon dioxide, the fulgenic acid yields colourless *αδ-dipiperonylbutane-βγ-dicarboxylic acid*,

$$CH_2\dot{:}O_2\dot{:}C_6H_3\cdot CH_2\cdot CH(CO_2H)\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_3\dot{:}O_2\dot{:}CH_2,$$

m. p. 228° (decomp.) after turning yellow at 210° and softening at 220°. With concentrated sulphuric acid it yields a pale red, and

ultimately a purple-red, coloration. A comparison is made between the colours of various acids containing phenyl and piperonyl groups.

XI. *Two Stereoisomeric α-Piperonyl-δ-phenyl-δ-methylfulgenic Acids.* —[With FERDINAND GADEMANN and ROBERT ROSE.]—Piperonaldehyde condenses with the ester of phenylmethyl*iso*itaconic acid in the presence of dry ether and sodium ethoxide at low temperatures, yielding as the only product *α-piperonyl-δ-phenyl-δ-methylfulgenic acid*, $\begin{matrix}C_6H_5\\CH_3\end{matrix}{>}C{:}C\!\!\begin{matrix}\diagup CO_2H & CO_2H\diagdown\\ \hline\end{matrix}\!\!C{:}C{<}\begin{matrix}C_6H_3{:}O_2{:}CH_2\\H\end{matrix}$, which crystallises from glacial acetic acid or water, has m. p. 196—198° (decomp.), and gives a malachite-green coloration with concentrated sulphuric acid. The corresponding *fulgide*, $C_{20}H_{14}O_5$, crystallises from glacial acetic acid in greenish-yellow needles, m. p. 159—161°. The ester of phenylmethylitaconic acid does not condense with piperonaldehyde so readily as its isomeride, and yields *α-piperonyl-δ-phenyl-δ-methyl*allo*fulgenic acid*, $\begin{matrix}CH_3\\C_6H_5\end{matrix}{>}C{:}C\!\!\begin{matrix}\diagup CO_2H & CO_2H\diagdown\\ \hdashline\end{matrix}\!\!C{:}C{<}\begin{matrix}C_6H_3{:}O_2{:}CH_2\\H\end{matrix}$, which crystallises from 50% acetic acid in colourless plates, m. p. 201—202° (decomp.). Its solution in concentrated sulphuric acid has a reddish-yellow colour. The corresponding *fulgide*, $C_{20}H_{14}O_5$, crystallises from glacial acetic acid in pale orange-coloured needles, m. p. 201—202°. In the preparation of the *allo*-acid, it is advisable to isolate the barium salt, and to extract this with alcohol before decomposing with hydrochloric acid, as small amounts of impurity interfere with the crystallisation of the acid.

XII. *α-Piperonyl-δ-naphthyl-δ-methylfulgide.* — [With ALFRED LENZNER.]—The α- and β-naphthyl methyl ketones condense with ethyl succinate in the presence of dry ether and sodium ethoxide at low temperatures, yielding the acid esters of *γ-(α- or β-)naphthyl-γ-methylitaconic acid*, $C_{10}H_7{\cdot}CMe{:}C(CO_2Et){\cdot}CH_2{\cdot}CO_2H$. The α-naphthyl compound crystallises from carbon disulphide in colourless prisms, m. p. 132°, and the corresponding dibasic *acid* has m. p. 168° (decomp.). The β-naphthyl derivative crystallises from a mixture of benzene and light petroleum, and has m. p. 103—104°; the corresponding dibasic *acid* has m. p. 165° (decomp.), and the *diethyl* ester, $C_{20}H_{22}O_4$, has b. p. 280—282°/64 mm. This ethyl ester condenses with piperonaldehyde at low temperatures in the presence of dry ether and sodium ethoxide, yielding the crude fulgenic acid, which, on treatment with acetyl chloride, yields *α-piperonyl-δ-2-naphthyl-δ-methylfulgide*,

$$C_{24}H_{16}O_5,$$

in the form of a dark orange-coloured powder.

XIII. *Triarylated Fulgenic Acids and Their Fulgides. Dyeing Experiments* (compare Abstr., 1904, i, 672; 1906, i, 91).—Good yields (80%) of triarylated fulgenic acids can be obtained by condensing aromatic aldehydes with ethyl diphenylitaconate in the presence of sodium ethoxide. The acids isolated are homogeneous, and do not consist of mixtures of stereoisomerides. The acids are yellow or orange-coloured, and the corresponding salts and esters are colourless or only slightly coloured. The corresponding fulgides are readily prepared, and are coloured red; they show pleochroism, and are

strongly phototropic. The product, obtained by the condensation of ethyl phenylitaconate and benzophenone, is a lactonic acid, and is only slowly transformed into the triphenylfulgenic acid when boiled with sodium ethoxide solution.

The di-, tri-, and tetra-arylated fulgides in the form of extremely fine suspensions in water are capable of dyeing wool, and in this respect resemble the dyes described by Vignon (Abstr., 1910, ii, 272, 273).

[With ERICH BENARY.]—$\alpha\delta\delta$-Triphenylfulgide yields a *dibromide*, $C_{24}H_{16}O_3Br_2$, which separates from carbon disulphide in yellow plates containing solvent of crystallisation; it loses the solvent on exposure to the air, turns a paler colour, and then has m. p. 129° (decomp.).

[With CURT KOHLMANN.]—*$\delta\delta$-Diphenyl-α-p-chlorophenylfulgenic acid*, $C_6H_4Cl\cdot CH\colon C(CO_2H)\cdot C(CO_2H)\colon CPh_2$, crystallises from 60% acetic acid in pale yellow needles, m. p. 242° (decomp.). The *sodium* salt crystallises in colourless plates containing alcohol, the *barium* salt is insoluble, and the *fulgide*, $C_{24}H_{15}O_3Cl$, crystallises in orange-red, triclinic prisms, m. p. 197°, and is strongly pleochroic.

[With GUSTAV REDDELIEN.]—The *methyl* ester of $\delta\delta$-diphenyl-α-*o*-methoxyphenylfulgenic acid separates from methyl alcohol in colourless crystals, m. p. 137°.

[With CURT KOHLMANN and GUSTAV REDDELIEN.]—*$\delta\delta$-Diphenyl-α-veratrylfulgenic acid*, $C_{26}H_{22}O_6$, crystallises from 60% acetic acid, has a very pale yellow colour, and melts at 154° (decomp.). The *sodium* salt is sparingly soluble in water, and crystallises from 80% alcohol; the *dimethyl* ester has m. p. 112°, and the *fulgide*, $C_{26}H_{20}O_5$, forms monoclinic plates, m. p. 164·5°.

[With CURT KOHLMANN, THEODOR BADENHAUSEN, and HARALD KALNING.]—*$\delta\delta$-Diphenyl-α-piperonylfulgenic acid*, $C_{25}H_{18}O_6$, crystallises from chloroform or benzene in pale yellow needles, m. p. 221° (decomp.), and the *fulgide*, $C_{25}H_{16}O_5$, forms red, monoclinic, pleochroic crystals, m. p. 201°. *$\delta\delta$-Diphenyl-α-piperonylbutane-$\beta\gamma$-dicarboxylic acid*, $CH_2O_2\colon C_6H_3\cdot CH_2\cdot CH(CO_2H)\cdot CH(CO_2H)\cdot CHPh_2$, crystallises from light petroleum in well-developed prisms, m. p. 182° (decomp.). The *anhydride* forms colourless, flat needles, m. p. 170—172°.

XIV. *Styrylfulgenic Acids and Fulgides.*—[With ERICH BENARY and SIEGFRIED SEYDEL.]—The styrylfulgenic acids are best prepared by the condensation of cinnamaldehyde with esters of substituted itaconic acids, and can be isolated in the anhydrous form or as compounds containing $1H_2O$, which is readily removed on gently heating.

$\delta\delta$-Diphenyl-α-styrylfulgenic acid,

$$CHPh\colon CH\cdot CH\colon C(CO_2H)\cdot C(CO_2H)\colon CPh_2,$$

has m. p. 212—214° (decomp.). It absorbs water readily, yielding the *acid*, $C_{26}H_{22}O_5$, m. p. 200°, after sintering at 150—160° when rapidly heated.

$\delta\delta$-Diphenyl-α-styrylfulgide, $C_{26}H_{18}O_3$, crystallises in ruby-red needles, m. p. 186—189°, and yields a *dibromide*, m. p. 167—168° (decomp.).

δ-Phenyl-α-styrylfulgide, $C_{20}H_{14}O_3$, separates from benzene in orange-coloured crystals, m. p. 126°, and *α-styryl-$\delta\delta$-dimethylfulgide*, $C_{16}H_{14}O_3$, forms large, golden-yellow crystals, m. p. 203°. The corresponding

fulgenic acid exists in two forms, melting respectively at 170—173° and 223°.

XV. *Diphenylenefulgenic Acids, the Isomeric Lactonic Acids, and Diphenylenefulgides.* — [With THEODOR BADENHAUSEN, RUDOLF HENNICKE, and EMIL WAHL.]—The diphenylenefulgenic acids are formed by the condensation of fluorenone with esters of substituted itaconic acids, but the conditions vary in the different condensations.

a-Phenyl-δ-diphenylenefulgenic acid is orange-coloured, has m. p. 206—208° (decomp.), and yields a *fulgide*, $C_{24}H_{14}O_3$, which crystallises from light petroleum in dark red needles, m. p. 182—183°. *γ-Phenyl-a-fluorenylparaconic acid*, $C_{12}H_8{:}C{:}\!<\!{\begin{matrix}CO\text{———}O\\CH(CO_2H)\end{matrix}}\!>\!CHPh$, crystallises in yellowish-green cubes, m. p. 193°.

aa-Diphenyl-δ-diphenylenefulgenic acid crystallises from benzene, has m. p. 201°, and yields a *fulgide*, $C_{30}H_{18}O_3$, with m. p. 269°.

δ-Diphenylene-aa-dimethylfulgenic acid, $C_{20}H_{16}O_4$, crystallises from dilute acetone in yellow plates, m. p. 208°. The *fulgide*, $C_{20}H_{14}O_3$, crystallises from ethyl acetate in orange-coloured needles, m. p. 180°, and when reduced yields a *dihydrofulgide*, $C_{20}H_{16}O_3$, in the form of colourless rods, m. p. 218°. J. J. S.

Complete Synthesis of Ethyl*apo*camphoric Acid. GUSTAV KOMPPA and O. ROUTALA (*Ber.*, 1911, **44**, 858—863).—If Blanc and Thorpe's contention that the methylation product of methyl diketo-*apo*camphorate is an *O*-methyl derivative is correct (Trans., 1910, **97**, 836), it is immaterial what alkyl group is introduced, because, being attached to oxygen, it will be eliminated by hydriodic acid. It will be seen, therefore, that the following synthesis of ethyl*apo*camphoric acid, in the course of which the ethyl group withstands the attack of hydriodic acid, renders Blanc and Thorpe's position still less tenable.

A methyl-alcoholic solution of methyl diketo*apo*camphorate is treated with cold methyl-alcoholic sodium methoxide; ethyl iodide is then added, and the mixture is boiled for twenty hours. The resulting ethyl and diethyl derivatives are separated by sodium carbonate, the former, after being liberated from the alkaline solution by dilute hydrochloric acid, being freed from unchanged methyl diketo*apo*camphorate by means of ethereal copper acetate, in which the copper derivative of methyl diketo*apo*camphorate is insoluble. *Methyl diketoethyl*apo*camphorate*, ${\begin{matrix}CO{-}CH(CO_2Me)\\|\\CO{\cdot}CEt(CO_2Me)\end{matrix}}\!>\!CMe_2$, m. p. 69—70·5°, obtained in this way, forms brilliant rhombohedra, and develops a reddish-brown coloration with aqueous alcoholic ferric chloride. Its solution in sodium hydrogen carbonate and a little sodium carbonate is reduced by 2·5% sodium amalgam in an atmosphere of carbon dioxide, yielding ultimately an amorphous glassy mass of *dihydroxyethyl*apo*camphoric acid,* which without further examination is heated on the water-bath for thirty hours with hydriodic acid, D 1·7, and red phosphorus, whereby *ethyldehydro*apo-*camphoric acid,* ${\begin{matrix}CH{=\!=}C(CO_2H)\\|\\CH_2{\cdot}CEt(CO_2H)\end{matrix}}\!>\!CMe_2$, m. p. 190—191°, is obtained

By heating this acid with hydrogen bromide in glacial acetic acid for twelve hours at 125°, and reducing the product with zinc dust and glacial acetic acid, the two stereoisomeric forms of ethyl*apo*camphoric acid are obtained. These are separated by treating them with acetyl chloride, dissolving the product in ether, and shaking the ethereal solution with aqueous sodium carbonate. trans-*Ethyl*apo*camphoric acid*, obtained from the sodium carbonate solution, is an oil. The ethereal solution contains the *anhydride*, m. p. 93° (corr.), of *cis*-ethyl*apo*camphoric acid; the cis-*acid* itself, $\begin{matrix}CH_2\text{—}CH(CO_2H)\\ |\\ CH_2\cdot CEt(CO_2H)\end{matrix}\!\!>\!CMe_2$, has m. p. 183·5—184°.

*Methyl 4-keto-5-ethoxy-3-ethyldehydro*apo*camphorate*,

$$\begin{matrix}C(OEt){:}C(CO_2Me)\\ |\\ CO\text{——}CEt(CO_2Me)\end{matrix}\!\!>\!CMe_2,$$

the diethyl derivative obtained in the ethylation of methyl diketo-*apo*camphorate, has b. p. 166—167°/9 mm., $D_{17\cdot5}^{17\cdot5}$ 1·1270, and $n_D^{17\cdot5}$ 1·48990, and does not give a coloration with ferric chloride.

C. S.

Tannins. IV. Galloyl-ellagic Acid. MAX NIERENSTEIN (*Ber.*, 1911, 44, 837—840).—*Tetragalloyl-ellagic acid*,

$$\begin{matrix}CO\cdot C_6H[O\cdot CO\cdot C_6H_2(OH)_3]_2\cdot O\\ |\qquad | \qquad\qquad\qquad\qquad |\\ O\text{—}C_6H[O\cdot CO\cdot C_6H_2(OH)_3]_2\cdot CO\end{matrix}$$

prepared by the interaction of ellagic acid in sodium hydroxide solution with tricarbomethoxygalloyl chloride, crystallises in small, yellow needles, m. p. 297—300°. It gives a bluish-green coloration with ferric chloride; on acetylation an amorphous powder is obtained. It is absorbed quantitatively by hide powder and casein, and precipitated by gelatin. Partial hydrolysis could not be effected.

E. F. A.

***N*-Alkylated Aldoximes.** JOHANNES SCHEIBER (*Ber.*, 1911, 44, 761—769. Compare Mills and Bain, Trans., 1910, 98, 1866).—All attempts to prepare *N*-alkylated aldoximes in optically active modifications have proved unsuccessful (compare Kipping and Salway, Trans., 1904, 85, 438).

[With H. FLEISCHMANN.]—The N-*benzyl* derivative of opianic acid aldoxime, $CO_2H\cdot C_6H_2(OMe)_2\cdot CH\!<\!\begin{matrix}N\cdot C_7H_7\\ |\\ O\end{matrix}$, obtained by condensing opianic acid with β-benzylhydroxylamine, crystallises from alcohol in colourless prisms, m. p. 153°. The *cinchonine* salt, $C_{36}H_{39}O_6N_3,3H_2O$, crystallises from water in long, brilliant, transparent needles, m. p. 97°; the anhydrous compound has m. p. 115—117°, and rapidly absorbs moisture on exposure to the air. The salt has $[\alpha]_D^{20}$ + 78·15° in alcoholic solution, and on treatment with ammonium hydroxide solution yields an inactive ammonium salt.

[With K. KLOPPE.]—It has not been found possible to obtain isomeric alkylated oximes by condensing β-benzyl- or β-phenyl-hydroxylamine with an optically active aldehyde, for example, helicin. N-*Benzylhelicinaldoxime*, $C_6H_{11}O_5\cdot O\cdot C_6H_4\cdot CH\!<\!\begin{matrix}N\cdot C_7H_7\\ |\\ O\end{matrix}\!,H_2O$, crystallises in

small, felted needles, m. p. 165°, and has $[\alpha]_D^{20}$ −56·82° in alcoholic solution. The corresponding *phenyl* derivative, $C_{19}H_{21}O_7N,H_2O$, forms small, colourless needles, m. p. 180°, and has $[\alpha]_D^{20}$ −59·27°; it rapidly absorbs water, yielding a *trihydrate*, m. p. 125°. When hydrolysed by emulsin, the phenyl derivative yields inactive *N*-phenylsalicylaldoxime (Plancher and Piccinini, Abstr., 1905, i, 705). N-*Phenyltetra-acetylhelicinaldoxime*, $C_6H_7O(OAc)_4\cdot O\cdot C_6H_4\cdot CH<{}^{NPh}_{O}$,H_2O, obtained by condensing tetra-acetylhelicin with β-phenylhydroxylamine, and also by the action of β-acetobromoglucose on the sodium derivative of phenylsalicylaldoxime, separates from benzene in colourless crystals, with m. p. 166°, and $[\alpha]_D^{20}$ −29·68°. J. J. S.

Hydroaromatic Compounds. Chloro-derivatives of Hydroaromatic Ketones and Semibenzenes. KARL AUWERS (*Ber.*, 1911, **44**, 788—809. Compare Abstr., 1907, i, 399—403).—Doubly unsaturated ketones of the type of 1-methyl-1-dichloromethyl*cyclo*hexadien-4-one form additive compounds with two or four atoms of chlorine, and these compounds react with alkalis, losing hydrogen chloride, and yielding chloro-derivatives of the original ketones. From these chlorinated ketones, for example, $O:C<{}^{CCl:CH}_{CH:CH}>CMe\cdot CHCl_2$, tertiary alcohols can be synthesised by means of magnesium alkyl iodides, and from the alcohols, alkylidenechloro*cyclo*hexadienes (semibenzenes) are obtained by the action of anhydrous formic acid. When heated, the alkylidene derivatives readily undergo molecular rearrangement, and by the wandering of the $\cdot CHCl_2$ group yield benzene derivatives of the type 3-chloro-4-ββ-dichloroethyltoluene. The position of the ring chlorine atom has been proved by the elimination of hydrogen chloride from this compound, and the oxidation of the resulting styrene derivative to 2-chloro-*p*-toluic acid.

5 : 6-*Dichloro*-1-*methyl*-1-*dichloromethyl*-Δ^2-cyclo*hexen*-4-*one*,

$$CO<{}^{CH=\!=\!=CH}_{CHCl\cdot CHCl}>CMe\cdot CHCl_2,$$

obtained by the action of dry chlorine gas or of a carbon tetrachloride solution on the corresponding hexadiene, forms glistening, regular crystals, m. p. 118—120° (decomp.). It is volatile with steam, and decomposes when kept for some time.

5-*Chloro*-1-*methyl*-1-*dichloromethyl*-$\Delta^{2:5}$-cyclo*hexadien*-4-*one*, $C_8H_7OCl_3$, crystallises from dilute methyl alcohol in small needles, m. p. 67°, b. p. 189·5—190°/22 mm., and yields a *semicarbazone*, $C_9H_{10}ON_3Cl_3$, in the form of compact, colourless needles, m. p. 181—182°, which are hydrolysed by 30% sulphuric acid.

3-*Chloro*-4-*hydroxy*-1 : 4-*dimethyl*-1-*dichloromethyl*-$\Delta^{2:5}$-cyclo*hexadiene*, ${}^{Me}_{CHCl_2}>C_6H_4<{}^{Me}_{OH}$, crystallises from light petroleum in colourless needles, m. p. 104°, and when shaken for ten minutes with eight to ten times its weight of concentrated formic acid yields 3-*chloro*-1-*methyl*-1-*dichloromethyl*-4-*methylene*-$\Delta^{2:5}$-cyclo*hexadiene*, $C_9H_9Cl_3$; this is transformed at 85° into 5-*chloro*-1-*methyl*-4-ββ-*dichloroethylbenzene*,

$C_9H_9Cl_3$, which is a colourless oil, b. p. 147·8—148·6°/19 mm., D_4^{20} 1·2873, n_a 1·54528, n_D 1·55012, n_β 1·56130, n_γ 1·57143.

2 : 3 : 5 : 6-*Tetrachloro*-1-*methyl*-1-*dichloromethyl*cyclo*hexan*-4-*one*, $C_8H_8OCl_6$, exists in two stereoisomeric modifications. The *trans*-compound is formed when the ketone is treated with a carbon tetrachloride solution of chlorine (3 mols.) in the presence of a little iron powder; it separates from light petroleum in regular crystals, m. p. 135—136° (decomp.), and is more stable than the dichloride. The *cis*-compound is formed when carbon disulphide is used as a solvent, and the solution exposed to light. It crystallises in brilliant cubes, has m. p. 176° (decomp.), and is not so soluble as the isomeride.

3 : 5-*Dichloro*-1-*methyl*-1-*dichloromethyl*-$\Delta^{2:5}$-cyclo*hexadiene*-4-*one*, $C_8H_6OCl_4$, obtained by warming gently either the *cis*- or *trans*-compound with alcoholic potassium hydroxide, or with an acetic acid solution of potassium acetate, crystallises from light petroleum in colourless, flat needles, m. p. 97°, and does not yield a semicarbazone. When reduced with zinc dust and acetic acid, it yields *o*-dichloro-*p*-cresol (Claus and Riemann, Abstr., 1883, 1111). 3 : 5-*Dichloro*-4-*hydroxy*-1 : 4-*dimethyl*-1-*dichloromethyl*-$\Delta^{2:5}$-cyclo*hexadiene*, $C_9H_{10}OCl_4$, exists in two stereoisomeric forms. The one crystallises from light petroleum in short, glistening, brittle needles, m. p. 104°, or with $\frac{1}{2}C_6H_6$ in glistening needles, m. p. 97—98°, the other crystallises from light petroleum, and has m. p. 60—70°. 3 : 5-*Dichloro*-1-*methyl*-1-*dichloromethyl*-4-*methylene*-$\Delta^{2:5}$-cyclo*hexadiene*, $C_9H_8Cl_4$, obtained by heating the hydroxy-compound with formic acid, has $D_4^{16\cdot7}$ 1·4084, n_a 1·57462, n_D 1·58005, and n_β 1·59387 at 16·7°.

3 : 5-*Dichloro*-4-*ββ*-*dichloroethyltoluene*, $C_6H_2Cl_2Me\cdot CH_2\cdot CHCl_2$, is a colourless oil, b. p. 158·5—159·5°/15 mm., and has D_4^{19} 1·3976, n_a 1·56306, n_D 1·56784, n_β 1·57991, and n_γ 1·59033 at 19°.

Ice-cold concentrated sulphuric acid transforms the alcohol (m. p. 104°) into 3 : 5-*dichloro*-2 : 4-*dimethylbenzylidene chloride*, $C_6HCl_2Me_2\cdot CHCl_2$, which crystallises from light petroleum in glistening needles, m. p. 44—45°.

The corresponding *aldehyde*, $C_6HCl_2Me_2\cdot CHO$, crystallises in long, opaque needles, m. p. 108—112°, and yields a *semicarbazone*, $C_{10}H_{11}ON_3Cl_2$, m. p. 231—232°. 3 : 5-*Dichloro*-2 : 4-*dimethylbenzoic acid*, $C_6HCl_2Me_2\cdot CO_2H$, crystallises in colourless, glistening plates, m. p. 191°, and its *methyl* ester in slender needles, m. p. 49°.

1 : 3-Dimethyl-1-dichloromethyl-$\Delta^{2:5}$-*cyclo*hexadiene-4-one yields a *dichloride* only, namely, 5 : 6-*dichloro*-1 : 3-*dimethyl*-1-*dichloromethyl*-Δ^2-cyclo*hexen*-4-*one*, $CO<\begin{matrix}CMe{=\!=}CH\\CHCl\cdot CHCl\end{matrix}>CMe\cdot CHCl_2$, which crystallises from hot alcohol in small, colourless needles, m. p. 100°. 5-*Chloro*-1 : 3-*dimethyl*-1-*dichloromethyl*-$\Delta^{2:5}$-cyclo*hexadiene*-4-*one*, $C_9H_9OCl_3$, crystallises from dilute alcohol in nacreous plates, m. p. 56°, and reacts with magnesium methyl iodide, yielding 5-*chloro*-4-*hydroxy*-1 : 3 : 4-*trimethyl*-1-*dichloromethyl*-$\Delta^{2:5}$-cyclo*hexadiene*, $C_{10}H_{13}OCl_3$, which crystallises from light petroleum in needles, m. p. 80°. When shaken with formic acid for half an hour, the alcohol yields 5-*chloro*-1 : 3-

dimethyl-1-*dichloromethyl*-4-*methylene*-$\Delta^{2:5}$-cyclo*hexadiene*, $C_{10}H_{11}Cl_3$, as a pale yellow oil, $D_4^{17\cdot3}$ 1·2693, n_α 1·56255, n_D 1·56812, and n_β 1·58230 at 17·3°.

5-*Chloro*-1 : 3-*dimethyl*-4-$\beta\beta$-*dichloroethylbenzene*,

$C_6H_2ClMe_2\cdot CH_2\cdot CHCl_2$,

is a yellow oil, b. p. 155°/17 mm., $D_4^{16\cdot1}$ 1·2622, n_α 1·54788, n_D 1·55278, n_β 1·56427, and n_γ 1·57091 at 16·1°, and reacts with alcoholic potassium hydroxide, yielding 6-ω-*dichloro*-2 : 4-*dimethylstyrene*,

$C_6H_2Me_2Cl\cdot CH\!:\!CHCl$,

which crystallises from methyl alcohol in slender needles, m. p. 38—38·5°. When oxidised it yields an aldehyde, and from the aldoxime, by the elimination of water, 6-*chloro*-2 : 4-*dimethylbenzonitrile*, C_9H_8NCl, is obtained. This forms brittle, glistening needles, m. p. 54°, and is identical with the nitrile obtained from 6-chloro-2 : 4-dimethylaniline. The corresponding *amide* has m. p. 167°. J. J. S.

Catalytic Hydrogenation of *cyclo*Pentanone. MARCEL GODCHOT and FELIX TABOURY (*Compt. rend.*, 1911, **152**, 881—883).—On hydrogenating *cyclo*pentanone in presence of reduced nickel at 125°, water is formed with *cyclo*pentane, *cyclo*pentanol (50%), and a ketone (40%) having an odour of menthol. The latter is probably α-cyclo*pentyl*-cyclo*pentanone*, $C_{10}H_{16}O$, arising by hydrogenation of an intermediate unsaturated ketone. It has m. p. −13°, b. p. 115—117°/12 mm., D^{16} 0·9801 ; the *oxime* has m. p. 75° ; the *semicarbazone*, m. p. 210°.

W. O. W.

Action of Light on Cinnamylideneacetophenone. HANS STOBBE and CONRAD RÜCKER (*Ber.*, 1911, **44**, 869—872. Compare Stobbe and Wilson, Trans., 1910, **97**, 1722).—When a saturated solution of cinnamylideneacetophenone in benzene or chloroform is exposed to sunlight, a white precipitate consisting of a bimolecular ketone and a resin is obtained after two to three days ; the same result is obtained by using a quartz mercury lamp, the precipitate in this case containing a larger proportion of the resin. The precipitate is recrystallised from a mixture of alcohol and chloroform, and is then repeatedly extracted with acetone, whereby the pure ketone, $(C_{17}H_{14}O)_2$, m. p. 192°, is obtained. By distillation in a vacuum, or by heating its solution in phenetole or phenylcarbimide at 140—180°, the bimolecular ketone is depolymerised, and yields, not the original ketone, but an isomeric iso*cinnamylideneacetophenone*, $C_{17}H_{14}O$, m. p. 235°.

The question whether the three ketones are interconvertible has not yet been satisfactorily answered. Chloroform solutions of the *iso*ketone and of the bimolecular ketone are more or less resinified by exposure to sunlight. When, however, a saturated solution of cinnamylideneacetophenone in chloroform is exposed to sunlight for about a month and the precipitate is removed, the mother liquor, after exposure to diffuse daylight for a year and a-half, contains the yellow *iso*cinnamylideneacetophenone, together with the bimolecular ketone.

C. S.

Preparation of Alkylanthraquinones from Alkylbenzoyl Chlorides and Aluminium Chloride. I. CHR. SEER (*Monatsh.*, 1911, **32**, 143—166).—When *m*-toluoyl chloride and aluminium chloride are heated at 130° for two hours, and finally at 130—140° for sixteen hours, the product is a mixture of, probably three, dimethylanthraquinones, the least soluble of which, m. p. 235—236°, is obtained in 19% yield by crystallisation from acetic acid and from nitrobenzene. This compound, which is identical with the substance obtained by Lavaux by the interaction of methylene chloride, toluene, and aluminium chloride, is also produced in the following manner: *m*-Toluoyl chloride and *m*-xylene in carbon disulphide yield with aluminium chloride m-*tolyl* m-4-*xylyl ketone*, $C_6H_4Me\cdot CO\cdot C_6H_3Me_2$, b. p. 315—320, which is converted, after being boiled for five days, into 2 : 6-dimethylanthracene, m. p. 243°; the latter is oxidised by chromic and acetic acids to the dimethylanthraquinone, m. p. 235—236°. A consideration of the author's and of Lavaux's methods of preparing the substance leads by the process of exclusion to the conclusion that the compound must be 2 : 6-dimethylanthraquinone; Dewar and Jones' supposed 2 : 6-dimethylanthraquinone (Trans., 1904, **85**, 212) is probably the 2 : 7-isomeride.

By nitration with concentrated sulphuric acid and potassium nitrate, 2 : 6-dimethylanthraquinone yields (?) 1 : 5-*dinitro*-2 : 6-*dimethylanthraquinone*, colourless needles, which is converted into the *diamino*-compound, m. p. 255—256°, dark red needles, by reduction with alkaline sodium hydrosulphide. 1 : 5-*Di-iodo*-2 : 6-*dimethylanthraquinone*, obtained in the usual way, forms orange-yellow needles, m. p. 273°.

Anthraquinone-2 : 6-dicarboxylic acid, conveniently obtained by boiling 2 : 6-dimethylanthraquinone with chromic and glacial acetic acids for sixty hours, forms a *chloride*, $C_{16}H_6O_4Cl_2$, m. p. 197—198°, from which the *amide*, $C_{16}H_{10}O_4N_2$, m. p. above 370°, is produced by alcoholic ammonia, and 2 : 6-*di-a-naphthoylanthraquinone*, $C_{36}H_{20}O_4$, m. p. 183—185°, by naphthalene and aluminium chloride in nitrobenzene at 75—80° after twenty hours. C. S.

Phenanthrene Series. XXX. Preparation of 4-Hydroxy- from 4-Nitro-phenanthraquinone. JULIUS SCHMIDT and OTTO SCHAIRER (*Ber.*, 1911, **44**, 740—745).—4-Hydroxyphenanthraquinone has been prepared from the corresponding nitro-compound (Schmidt and Austin, Abstr., 1904, i, 69) by reduction with tin and hydrochloric acid, diazotising, and warming with water.

4-*Nitrophenanthraquinonedioxime*, $C_{14}H_9O_4N_3$, separates from alcohol in pale yellowish-green crystals, m. p. 210° (decomp.).

4-*Aminophenanthraquinone*, $NH_2\cdot C_6H_3<{CO-\atop C_6H_4}>CO$, is a black powder with a red lustre, has no definite m. p., and irritates the nasal mucous membrane. The *hydrochloride* of 4-*aminophenanthraquinol*,

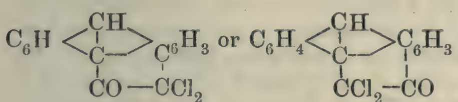
$$C_{12}H_{12}O_2NCl,$$

obtained by the reduction of the nitroquinone, crystallises in colourless plates, and turns brown during the process of drying. The most

characteristic derivative of the aminoquinone is the 4-*aminophenanthraphenazine*, $\begin{matrix} NH_2\cdot C_6H_3\cdot C:N \\ C_6H_4\cdot C:N \end{matrix}>C_6H_4$, the hydrochloride of which separates from water as a pale greyish-green, crystalline powder, m. p. 274—275° (decomp.). The *base* forms an olive-green, crystalline powder, m. p. 190° (not sharp).

4-*Hydroxyphenanthraquinone* forms a red powder, m. p. 285°. The *acetyl* derivative, $C_{16}H_{10}O_4$, separates from alcohol in pale brown, nodular masses, m. p. 188—189°. 4-*Hydroxyphenanthraquinonesemicarbazone*, $C_{15}H_{11}O_3N_3$, forms brownish-red crystals, m. p. 258° (decomp.), and 4-*hydroxyphenanthraphenazine*, $C_{20}H_{12}ON_2$, dark red, microscopic crystals, m. p. 233° (decomp.). J. J. S.

Derivatives of Aceanthrenequinone. CARL LIEBERMANN and MILAN ZSUFFA (*Ber.*, 1911, **44**, 852—858. Compare this vol., i, 202).—The following compounds show that an extensive parallelism exists between aceanthrenequinone and acenaphthenequinone. Aceanthrenequinone, which is purified best by means of its compound with sodium hydrogen sulphite, is oxidised by chromic acid to anthraquinone-1-carboxylic acid, m. p. 293—294° (corr.). By distillation with zinc dust it yields impure aceanthrene, m. p. 115—140°. By treatment with phosphoryl chloride and phosphorus pentachloride it yields *dichloroaceanthrenone* (annexed formula), yellow needles, m. p. 182—184°.



"*Aceanthren-2-indole-indigotin*" [*Indoxylaceanthrenone*],

$$C_{14}H_8<\begin{matrix} CO\ \ CO— \\ C{=}C\cdot NH \end{matrix}>C_6H_4,$$

m. p. 266°, brown needles, obtained by heating aceanthrenequinone and indoxyl in glacial acetic acid containing a little hydrochloric acid, gives a brown coloration with concentrated sulphuric acid, which changes to grey and then to blue. "*Aceanthren-2-thionaphthen-indigotin*" [*Oxythionaphthenylaceanthrenone*], $C_{14}H_8<\begin{matrix} CO\ \ CO \\ C{=}C\cdot S \end{matrix}>C_6H_4$, is prepared in a similar manner from hydroxythionaphthen (compare Friedländer and Bezdzik, Abstr., 1908, i, 673).

Azonium bases are readily obtained by the interaction of aceanthrenequinone and semidine bases. Thus, the quinone and 5-ethoxy-2-aminodiphenylamine hydrochloride in boiling glacial acetic acid yield, by the addition of a little hydrochloric acid, *ethoxyphenylaceanthraphenazonium chloride*, $C_{14}H_8<\begin{matrix} C:NPhCl \\ C:N—— \end{matrix}>C_6H_3\cdot OEt$, a dark green, metallic mass; the corresponding *nitrate* forms reddish-brown needles. *Ethoxyphenylacenaphthaphenazonium chloride*,

$$C_{10}H_6<\begin{matrix} C:NPhCl \\ C:N—— \end{matrix}>C_6H_3\cdot OEt,$$

prepared in a similar manner from acenaphthenequinone for the purpose of comparison, forms brownish-yellow needles, and dyes wool

yellow; the preceding anthracene derivative dyes wool a dirty ponceau-red.

Diphenylaceanthrene glycol, $C_{14}H_8<\begin{matrix}CPh\cdot OH\\ | \\ CPh\cdot OH\end{matrix}$, m. p. 160—162°, pale yellow needles, obtained from aceanthrenequinone and magnesium phenyl bromide, is converted by concentrated hydrochloric and glacial acetic acids into *diphenylaceanthrenone*, $C_{14}H_8<\begin{matrix}CO\\ | \\ CPh_2\end{matrix}$, m. p. 215—217°, yellow needles (compare Beschke and Kitaj, Abstr., 1909, i, 917).

Diphenyl-4-carboxylic acid, $CO_2H\cdot C_6H_4\cdot C_6H_5$, m. p. 224°, obtained by heating diphenyl, oxalyl chloride, and aluminium chloride in carbon disulphide, is best purified by means of its sparingly soluble *sodium* salt. *Retenecarboxylic acid*, $C_{18}H_{17}\cdot CO_2H$, prepared and purified in a similar manner, has m. p. 121—123°. Xanthone yields a *dicarboxylic acid*, $C_{13}H_8O(CO_2H)_2$, m. p. above 265°, under similar conditions.

C. S.

Oxidation of Camphene. GUSTAV KOMPPA (*Ber.*, 1911, **44**, 863—865).—When preparing *apo*camphoric acid by the oxidation of camphene by nitric acid, the author has always obtained an acid which does not yield an anhydride by treatment with acetyl chloride, and which he has always regarded as *trans-apo*camphoric acid. By further examination, however, the acid, which has the composition $C_{10}H_{14}O_3$, and m. p. 233·5—234·5°, and forms a phenylhydrazone, m. p. 146°, proves to be ketopinic acid.

This discovery is of interest, because now all of the compounds—campheneglycol, hydroxycamphenylanic acid, tricyclenic acid, hydroxy-*apo*camphanecarboxylic acid, ketopinic acid, carboxy*apo*camphoric acid—which represent the successive steps in the oxidation of camphene to *apo*camphoric acid, have, with the exception of hydroxy*apo*camphan-carboxylic acid, been isolated from the products of oxidation of camphene.

C. S.

Components of Essential Oils. "False Camphor Wood Oil" (faux camphrier). Natural Occurrence of Myrtenal and *d*-Perilla Aldehyde. FRIEDRICH W. SEMMLER and B. ZAAR (*Ber.*, 1911, **44**, 815—819).—False camphor wood oil, in addition to *d*-limonene and cineol, consists mainly of an aldehyde, $C_{10}H_{14}O$, b. p. 99—104°/9 mm., D^{18} 0·965, n_D 1·50803, $[\alpha]_D$ + 135·6°, which is the optical isomeride of *l*-perilla aldehyde. In addition the oil contains a dicyclic aldehyde, $C_{10}H_{14}O$, identical with the synthetical myrtenal (Semmler and Bartelt, Abstr., 1907, i, 429). This is the first occurrence of myrtenal in an essential oil. Myrtenal and perilla aldehyde are related in the same manner as pinene and limonene, and the occurrence of both in the same oil is remarkable.

E. F. A.

Oil of Thea Sasanqua. H. KIMURA (*Ber. Deut. Pharm. Ges.*, 1911, **21**, 209—212).—The young leaves of the Japanese *Thea Sasanqua* are steeped in water for twenty-four hours and then distilled

with steam. The oil, the yield of which varies from 0·4—1·0%, according to the period elapsing between the gathering of the leaves and their treatment (no oil is obtained after three months' keeping), is optically inactive, has a sweet, pleasant odour, and D^{21} 1·061. It contains about 97% of eugenol, a very small amount of an aldehydic or ketonic substance, and an ester. By hydrolysis with 2% alcoholic potassium hydroxide, the ester yields an alcohol with the odour of geraniol and a malodorous acid; these are being further examined. C. S.

Hydrogenation of Turpentine Oil. GUSTAVE VAVON (*Bull. Soc. chim.*, 1911, [iv], 9, 256—261. Compare Darmois, Abstr., 1908, ii, 747; 1910, i, 52).—The hydrogenation of French, German, and American turpentine oils has been studied, and it is shown that (1) these all consist of α- and β-pinenes; (2) the two pinenes yield the same hydrocarbon on reduction; (3) sophistication of turpentine oil may be detected by (*a*) fractionation and (*b*) reduction and examination of the resulting products.

One hundred and thirty-six grams of the fraction of turpentine oil boiling at 155—165°, on reduction with platinum-black in presence of hydrogen, absorbs 1 gram-mol. of hydrogen, giving a *hydrocarbon*, $C_{10}H_{18}$, b. p. 166°, m. p. $-50°$, D^{15}_{15} 0·861, and $[\alpha]$ $+23·8°$ to $-23·8°$ for $\lambda=578$, depending on the source of the oil used.

The relationship between the rotations of fractions of the same turpentine oil and those of the same fractions after reduction, indicates that the three oils examined consist essentially of α-pinene and β-pinene. The latter has b. p. 164°, m. p. $-50°$, $\alpha_J=39·6°$, and on reduction gives a hydrocarbon having $\alpha_J=-40·6°$. α-Pinene on reduction gives a hydrocarbon having $\alpha_J=+41°$. French, German, and American turpentine oils contain respectively 63, 23, and 72% of α-pinene, consisting of the two optically inverse forms in varying proportions.

A pure turpentine oil should consist of at least 80%, boiling below 164°, and that portion boiling from 155—158° on hydrogenation by platinum-black should give a hydrocarbon boiling constantly at 166°. The platinum-black may be used several times without losing its activity if it is washed with ether after each operation and heated for a few minutes at 200°. T. A. H.

Caoutchouc Nitrosites and their Application in Analysis. PAUL ALEXANDER (*Zeitsch. angew. Chem.*, 1911, 24, 680—687. Compare Abstr., 1907, i, 433).—This paper is devoted mainly to a criticism of a communication on this subject by Gottlob (Abstr., 1908, i, 95). The author brings forward fresh evidence in support of his contention that a nitrosite having the composition

$$C_{10}H_{15}O_7N_3$$

cannot be obtained directly from caoutchouc, as stated by Gottlob (*loc. cit.*) and Harries (compare Abstr., 1905, i, 223). The nitrosite formed directly from the interaction of nitrous fumes and caoutchouc approximates to the formula $C_9H_{12}O_6N_2$, but is not to be regarded as a simple substance. The production of carbon dioxide during the reaction has been verified, and it has been demonstrated also that the

same gas is liberated when the crude nitrosite is heated at 40—80°; in fact, it has been possible to absorb about 87% of the one molecular proportion of carbon dioxide evolved from one molecular proportion of caoutchouc. In conclusion, the author states that this reaction may be employed for the analysis of crude caoutchoucs, and, in many cases, also for the estimation of caoutchouc in vulcanised rubber products. W. H. G.

Cold Vulcanisation. B. V. Bysoff (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 209. Compare Abstr., 1910, i, 865; this vol., i, 314).—Comparative measurements have been made of the amount of sulphur which is fixed when dry caoutchouc is vulcanised by means of dry and moist benzene solutions of sulphur chloride. In two pairs of experiments with benzene solutions containing 0·5 and 1·0 gram of sulphur chloride per 100 c.c., it was found that the amount of fixed sulphur in the vulcanisation with the moist solution was only 76 (77) % of that fixed when the dry solution was employed. With undried caoutchouc and a dry benzene solution a similar reduction of the amount of fixed sulphur was observed. H. M. D.

Behaviour of Colloidal Metals (Platinum, Gold, Silver, and Palladium) Prepared by Bredig's Method on Solutions of Guaiaconic Acid. George A. Buckmaster (*7th Intern. Congr. Appl. Chem.*, Sect. IV A 2, 29).—Guaiaconic acid in oxygen-free alcohol is oxidised to guaiacum-blue by colloidal metals prepared by Bredig's method, for the particles of metal contain occluded or adsorbed oxygen. A given weight of any of these colloidal metals oxidises a definite amount of guaiaconic acid. The metallic sol is then inactive, but may be reactivated by air or oxygen. Gold sol, when first prepared, is active for a few hours, but rapidly loses the property, which is preserved for weeks and months by the sols of platinum, palladium, and silver. The occluded oxygen of platinum sols can be driven out by boiling, or by the passage of pure hydrogen or carbon dioxide, and the inactive sols obtained can be reactivated by oxygen. The oxidation of guaiaconic acid is therefore due, not to the colloidal metal as such, but to the occluded oxygen. The action of platinum-black on guaiaconic acid is similarly due to occluded oxygen.

R. V. S.

The Pseudo-Peroxydase Reaction between Hæmoglobin its Derivatives, and Guaiaconic Acid (Guaiacum Reaction for Blood Pigment). George A. Buckmaster (*7th Intern. Congr. Appl. Chem.*, Sect. IV A 2, 30).—The oxidation of guaiaconic acid, aloin, or leucomalachite-green in the presence of traces of hydrogen peroxide is effected by minute amounts of hæmoglobin or any of its derivatives which contain iron. Pure hæmatoporphyrin or hæmatoidin (that is, iron-free derivatives) are incapable of causing the oxidation of these substances. Blood solutions which have been heated in a sealed tube at 200° for three hours still give the reaction. The reaction is therefore not due to a peroxydase, but is connected with the presence of the iron contained in the hæmoglobin. R. V. S.

The Sugar in Sophorin. HENRI TER MEULEN (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 411—415).—A sugar has been isolated from sophorin, a glucoside present in the flower-buds of the Chinese yellow currant (*Sophora japonica*), and proved to be identical with rhamninose, although it was not obtained pure. Sophorin was treated with rhamninase solution for a day at 60°, the mixture filtered, and, after concentration at reduced pressure, the filtrate boiled with alcohol to destroy the enzyme. Fractional precipitation with ether yielded a light yellow syrup. With the polarimeter a rotation of $-3°29'$ was observed, the theoretical value for the same quantity of rhamninose being 3°36′. Sophorin is probably identical with rutin. A. J. W.

Balanophorin. I. M. SIMON (*Monatsh.*, 1911, **32**, 89—104).—Brief references are given to previous investigations of balanophorin, the waxy substance obtained from the *Balanophorae*. It is extracted by ether from the dried Javanese tubers, and purified by successive treatment with alcohol and acetone. The purified substance, $C_{12}H_{20}O$(?), is a white, amorphous powder, has m. p. 56—57°, and is not decomposed by aqueous or alcoholic alkalis even at 140°. By distillation under 19 mm., or by fusion with potassium hydroxide at 150—210°, it yields palmitic acid and other products as yet unexamined. C. S.

Dye in the Root of Azafran. CARL LIEBERMANN (*Ber.*, 1911, **44**, 850—851).—The root of a plant obtained from Paraguay, and belonging to the family of the Scrophulariaceæ, is used under the name azafran or azafranillo to colour fats. It contains about 1% of a dye, called *azafrin*, which is easily extracted by boiling benzene. From the solution the dye is obtained in orange-red crusts, which form microscopic needles, m. p. 214°, after recrystallisation. It does not contain nitrogen or methoxy- or ethoxy-groups, but the presence of one hydroxyl group is shown by Zerewitinoff's method. It dyes wool yellow, and forms yellow to orange lakes with Scheurer's mordants, but not with the usual mordants; wool extracts the whole of the dye from a hyposulphite vat. The dye gives a fine blue solution in concentrated sulphuric acid, which becomes violet by the addition of alcohol. The examination of the dye is being continued. C. S.

Chlorophyll. XIII. Decomposition and Formation of Chlorophyll. RICHARD WILLSTÄTTER and ARTHUR STOLL (*Annalen*, 1911, **380**, 148—154).—In continuation of the previous work (this vol., i, 141), it is shown that chlorophyllase has synthesising properties, and can build up chlorophyll from phytol and chlorophyllide.

The method consists in hydrolysing chlorophyll, for example, by digesting the meal from leaves of *Gallopsis* with moist ether for several days, then adding phytol, and in the course of several days one-third to three-fourths of the original chlorophyll is regenerated. This confirms the view that the enzyme plays an important function

in the formation of chlorophyll in plant tissues. The chlorophyll obtained yields the same phytochlorin-*e* and phytorhodin-*g* as are obtained from natural chlorophyll.

It is also shown that chlorophyllase can esterify chlorophyllide in the presence of ethyl alcohol, yielding ethyl chlorophyllide. J. J. S.

Chlorophyll. XIV. Comparative Experiments with Chlorophyll from Different Plants. III. RICHARD WILLSTÄTTER and MAX ISLER (*Annalen*, 1911, **380**, 154—176. Compare Willstätter, Hocheder, and Hug, Abstr., 1910, ii, 150; Willstätter and Oppé, this vol., i, 140).—The solution of the question as to the identity of the chlorophyll obtained from different plants has been attempted by an examination of the phytochlorins and phytorhodins obtained by their decomposition. Previous experiments have indicated that in the great majority of cases the products obtained from dried leaves are phytochlorin-*e* and phytorhodin-*g*, although several exceptions had been met with. It is shown in the present communication that these exceptions are due, not to differences in the natural phytochromin, but to the methods of treatment of the material producing alterations in the chlorophyll. All these exceptions disappear when the dried material is extracted, the chlorophyll solution immediately treated with acid, and the resulting phæophytin hydrolysed in the cold with alkali. Under these conditions the dried leaves of all varieties of plants yield only phytochlorin-*e* and phytorhodin-*g*.

If the filtered chlorophyll extract is kept, the phytochromin undergoes change, especially in the case of the extract from stinging nettles, and the final products of decomposition are phytochlorin-*f*, which is soluble in 11% hydrochloric acid, and a phytorhodin with feebler basic properties than phytorhodin-*g*. Of extreme importance is the sensitiveness of phytorhodin towards alkali, the longer the product is left in contact with warm alkali the smaller is the yield of phytorhodin. If, however, this source of error is avoided, the relative molecular proportions of phytorhodin to phytochlorin are approximately 1 : 2·5.

Experiments have been made with fresh vegetable tissues as well as with dried, and the investigation is complicated by the fact that during the processes of dividing and extracting large quantities of the material fermentative changes of a complex nature can take place. For example, in the case of grass, phytochlorin-*f* is obtained, whereas dry grass gives the normal product, phytochlorin-*e*.

The best method of treating the fresh tissue is the addition of aqueous methyl alcohol, by means of which the division and extraction of the material is greatly facilitated. Under these conditions, provided the extraction is made immediately after the addition of the alcohol, the phæophytin obtained yields in all cases the normal products of decomposition, namely, phytochlorin-*e* and phytorhodin-*g*, and in practically the same proportion as obtained from dry leaves.

The question as to whether the phytochlorin and phytorhodin are derived from the same molecule of chlorophyll and phæophytin is discussed, and the conclusion is drawn that in all probability they are derived from different molecules, so that chlorophyll consists of two components, one of which gives rise to phytochlorin and the other to

phytorhodin (compare Tsvett, Abstr., 1907, i, 787). The amounts of phytochlorin-*e* and phytorhodin-*g* obtained from a given quantity of phæophytin by the action of alcoholic potassium hydroxide were estimated colorimetrically by comparison with known quantities of the pure substances.

The fresh material examined included leaves of the following: *Hyloconium*, *Aspidium*, *Equisetum Pinus*, *Salix*, *Urtica*, *Platanus*, *Rubus*, *Buxus*, *Aesculus*, *Petroselinum*, *Heracleum*, *Galeopsis*, *Solanum*, and *Sambucus*. J. J. S.

Chlorophyll. XV. Isolation of Chlorophyll. Richard Willstätter and Ernst Hug (*Annalen*, 1911, 380, 177—211).—The object of the investigation has been the isolation of pure chlorophyll. It occurs in plant tissues mixed with yellow pigments, for example, carotin and xanthophyll, and with fats, waxes, and salts of aliphatic acids. Many of these distribute themselves between solvents in much the same manner as chlorophyll itself, and their removal is tedious. The presence of these impurities always reduces the magnesium contents of the colouring matter, and is indicated by the presence of calcium compounds in the ash derived from the specimen.

The chlorophyll was always extracted from dried leaves, and estimated colorimetrically by Willstätter, Hocheder, and Hug's method (Abstr., 1910, ii, 151) by comparison with ethylchlorophyllide solutions of known concentration. The expression, degree of purity, is used to express the percentage of chlorophyll in 100 grams of dried extract when heated for a half to three-quarters of an hour under reduced pressure.

Although the amount of chlorophyll extracted is greater the longer the extraction is carried out, it is inadvisable to prolong the period of extraction, as the chlorophyll can undergo alteration during this time (compare Willstätter and Oppe, this vol., i, 141, and Willstätter and Isler, preceding abstract). To obtain unaltered chlorophyll it is essential that the extraction should be rapid, although the amount extracted is not so large. The method used is a modification of that of Willstätter and Stoll (this vol., i, 142), and consists in spreading the dried meal on the thimble before the addition of the solvent. With a charge of 2 kilos. the extraction requires two to three hours, and the volume of solvent is about 1·5 litres per kilo. of meal. Using ethyl alcohol, the degree of purity of the extract is about 14—16, as the chlorophyll contains about six times its own weight of impurities. Before treatment with alcohol it is an advantage to subject the meal to a preliminary extraction with benzene (3 litres) and then light petroleum (1·5 litres per kilo.). The light petroleum is essential in order to remove the benzene, and it is not necessary to dry the meal after extraction with the different solvents. This preliminary extraction increases appreciably the degree of purity of the subsequent crude solution in light petroleum.

To obtain such a solution, the alcoholic extract is shaken with two-thirds its volume of light petroleum and one-third its volume of water. Fractional extraction offers no advantages, and the degree of purity of

the solution is usually 33—40, provided the preliminary extraction with benzene and light petroleum is carried out. By twice washing the light petroleum solution with aqueous methyl alcohol (90%) it is possible to increase the degree of purity to 50—60. It is essential that the alcohol should not be too concentrated, as considerable amounts of chlorophyll are then removed. The degree of purity can be increased to 70 by extracting the washed light petroleum solution twice with 95% methyl alcohol saturated with light petroleum (b. p. 30—50°), when about half the chlorophyll is dissolved by the alcohol. The alcoholic solution is finally shaken with light petroleum, and to obtain the chlorophyll from this final light petroleum solution (purity 70), it is washed with water until free from methyl alcohol, when the pigment is precipitated in a very fine state of division which cannot be filtered. The addition of large amounts of anhydrous sodium sulphate, or of smaller amounts and a little calcium carbonate, renders the precipitation complete, and also deposits the precipitate in such a form that it can be filtered with ease. To purify the chlorophyll it is dissolved in 96% alcohol, precipitated with dilute sodium chloride solution, and finally dissolved in ether and precipitated with light petroleum. The yield is 0·75 to 1 gram from 2 kilos. of stinging nettle meal containing 14—16 grams of chlorophyll.

A pure specimen should possess the following characteristics:

1. The ash must correspond with the theoretical, and consist of pure magnesium oxide.

2. The phytol content must be 33%, and the phytol must be free from solid impurities.

3. During the hydrolysis with alkalis the temporary formation of the brown coloration must be given.

4. By the decomposition of the phæophytin, the normal products, phytochlorin-*e* and phytorhodin-*g*, must be formed.

5. The specimen must contain no yellow pigments.

6. The spectrum must correspond with that of the chlorophyll in the leaf extract.

The pure compound is a bluish-black, glistening powder with a metallic lustre, and when finely divided gives a greenish- or bluish-black powder. It appears crystalline under the microscope, and has no definite m. p.; for example, different specimens melt at 93—96° or 103—106° when heated in ordinary m.-p. tubes. Its ethereal solution has a brilliant greenish-blue colour, and is strongly fluorescent. It is practically insoluble in cold light petroleum, but dissolves readily on the addition of a few drops of methyl or ethyl alcohol. It is also soluble in benzene and pyridine, and its alcoholic solution gives Kraus's reaction. The pigment has neither acid nor basic properties, but is readily decomposed by both acids and alkalis. Analyses agree with the formula $C_{55}H_{72}O_6N_4Mg$. Its absorption spectrum is analogous to that of ethyl chlorophyllide, and it undergoes alcoholysis or hydrolysis in the presence of chlorophyllase (compare this vol., i, 141).

The chlorophyll thus obtained is a mixture of two components (compare Willstatter and Isler, preceding abstract), which have been isolated and will be described later. J. J. S.

The Existence of Two Chlorophyllans. M. TSVETT (*Biochem. Zeitsch.*, 1911, 31, 505—506).—The author maintains as a result of his adsorption-spectroscopic analytical researches that two chlorophyllans exist, as also two chlorophyllins. S. B. S.

A New Vegetable Colouring Matter: Thujorhodin. M. TSVETT (*Compt. rend.*, 1911, **152**, 788—789).—The leaves of *Thuja orientalis*, as well as of other Coniferæ (*Cryptomeria japonica, Juniperus virginiaca, Taxus baccata*, etc.), after grinding with sand and calcium carbonate, yield a new colouring matter on extraction with carbon disulphide or light petroleum. This substance, for which the name *thujorhodin* is proposed, gives the lipochrome blue coloration with concentrated sulphuric acid. The solution in carbon disulphide is red, and shows four absorption bands, λ 570—560, 530—515, 470—475 [?455], 450—440. The alcoholic solution is rose-coloured, and shows less distinct bands, whilst three bands are visible in the light petroleum solution, which is yellow. W. O. W.

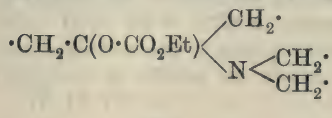
Separation of Urobilin from its Chromogen. LÉON GRIMBERT (*Compt. rend.*, 1911, **152**, 727—728).—The fresh urine is extracted with chloroform. After filtering the chloroform through cotton wool, an alcoholic solution of zinc acetate is added until the turbidity first formed disappears; the appearance of a green fluorescence indicates the presence of free urobilin. In this case the chloroform is shaken with a few c.c. of aqueous sodium phosphate neutral to phenolphthalein. This removes only the chromogen of urobilin (Saillet's urobilinogen). The chloroform layer now gives the fluorescence only after treatment with a trace of iodine or other oxidising agent. The chromogen cannot be extracted by chloroform from solutions which are alkaline to phenolphthalein. W. O. W.

Isomeric Disulphoxides from Thianthren. KARL FRIES and WILHELM VOGT (*Ber.*, 1911, **44**, 756—761).—The products described by Krafft and Lyons (Abstr., 1896, i, 297) as thianthren dioxide and thianthrenmonosulphone are shown to be isomeric disulphoxides. Both are readily reduced to thianthren by hydrogen bromide at the ordinary temperature, or by warming with zinc dust and acetic acid, whereas sulphones are not attacked by hydrobromic acid. The compounds possess basic properties, and are not oxidised by nitric acid, whereas thianthrenmonosulphone is not basic, and is readily oxidised to a trioxide.

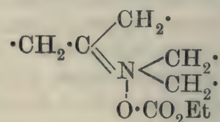
*iso*Thianthren disulphoxide crystallises readily from benzene in slender needles, and from water or glacial acetic acid in prisms, m. p. 249°. It dissolves in concentrated nitric or hydrochloric acid, yielding colourless solutions, and is transformed into the isomeric disulphoxide when heated for some time at 250° or more readily at 280°. The same transformation occurs when the *iso*-compound is dissolved in concentrated sulphuric acid, kept for two days, and then poured into water. Thianthren disulphoxide is most easily prepared by the action of chlorine on a benzene solution of thianthren, and has m. p. 284° (Krafft and Lyons: 278—279°). It is less soluble than the *iso*-compound in glacial acetic acid and in hydrochloric or nitric acids. Its

solution in concentrated sulphuric acid has a reddish-violet colour, and when this solution is kept for two days and then diluted with water, a mixture of the two isomeric disulphoxides is obtained. J. J. S.

Quinine and Euquinine. A. Astruc and L. Courtin (*J. Pharm. Chim.*, 1911, [vii], 3, 292—294. Compare Astruc, *Bull. Soc. chim.*, 1907, [iv], 1, 192).—The authors briefly recapitulate the points of similarity and difference between quinine aud euquinine; the most important difference is the fact that euquinine behaves as a mono-acidic base. The formation of euquinine by the attack of ethyl chloroformate on the hydroxyl group in the quinine molecule leads to a constitution containing the group (I). This constitution is not in



(I.)



(II.)

harmony with the stability of euquinine, or with its monobasic nature. The authors suggest that a constitution containing the group (II) is in better agreement with the facts. C. S.

Ephedrine and ψ-Ephedrine. Paul Rabe (*Ber.*, 1911, 44, 824—827).—Ephedrine and ψ-ephedrine are optically isomeric β-methylamino-α-phenylpropane-α-ols of the formula

OH·CHPh·CHMe·NHMe.

The ammonium base of ephedrine decomposes into water, methylamine, and α-phenylpropylene $\alpha\beta$-oxide, b. p. 204°, $[\alpha]_D^{16}$ +65·84°.

This oxide, when heated with aqueous methylamine in sealed tubes on the water-bath, forms the hydrochloride, $C_{10}H_{15}ON,HCl$, which melts partly at 148—149°, the rest at 165°, and has $[\alpha]_D^{19}$ +24·2°. It is a mixture of methylated $\alpha\beta$-hydramines. E. F. A.

New Leucomaine. J. Ubeda y Correal (*7th Intern. Congr. Appl. Chem.*, Sect. IV A 2, 112—113).—On treating 29 kilograms of fresh beef with water containing hydrochloric acid, a solution is obtained from which, by evaporation to dryness, extraction with alcohol, precipitation with mercuric chloride, and subsequent decomposition with hydrogen sulphide, a substance can be prepared which yields a platinichloride crystallising in red, acicular prisms (angles 48°49′ and 131°16′ respectively), and containing 47·22—47·31% of platinum. When the platinichloride is decomposed with hydrogen sulphide, a solution is obtained which reacts with gold chloride, picric acid, potassium and cadmium iodides, and other reagents. The hydrochloride forms colourless crystals (angles 31°33′ and 148°27′ respectively).

R. V. S.

Luciferesceine, the Fluorescent Material Present in Certain Luminous Insects. F. Alex. McDermott (*J. Amer. Chem. Soc.*, 1911, 33, 410—416).—Coblentz (*Physikal. Zeitsch.*, 1909, 10, 955) has

discovered that the firefly (*Photinus pyralis*) contains a substance which gives solutions with a bright blue fluorescence. More recently, he has found that *Photinus corruscus* and *Photuris pennsylvanica* also contain this substance.

The author has detected it in *Photinus pyralis*, *P. corruscus*, and also in *P. scintillans*, but has been unable to confirm its presence in *Photuris pennsylvanica*. It is particularly abundant in a sticky fluid which the insects emit when irritated. This substance, *luciferesceine*, can be obtained in an impure condition from an alcoholic extract of the insects, or, in a purer form, by dissolving in alcohol the sticky liquid on the walls of the vessels in which the insects have been confined. The alcoholic solution thus obtained is clear, colourless, has a bright blue fluorescence, and, on evaporation, yields a pale yellow, amorphous residue of luciferesceine. The compound gives a red coloration with concentrated sulphuric acid, and a dense, cream-coloured precipitate with potassium ferrocyanide. In general, its reactions indicate that it is probably of an alkaloidal nature. It seems likely that luciferesceine is contained in a defensive secretion of the insect, but that its fluorescence does not bear any relation to the vital processes or to the defensive function. E. G.

Preparation of ψ-Morphine by Mineral Catalysis. GEORGES DENIGÈS (*Bull. Soc. chim.*, 1911, [iv], 9, 264—266).—Ten c.c. of a 4% solution of copper sulphate, just decolorised with potassium cyanide, is poured into a solution containing 5 grams of morphine hydrochloride and 20 c.c. of hydrogen peroxide (10 to 12 vols.) in 200 c.c. of water. After a few minutes, oxygen is evolved and a precipitate of ψ-morphine, which soon becomes crystalline, is formed. The alkaloid may be purified by dissolving it in ammonia solution (22° B), decolorising with animal charcoal, and finally evaporating to a small bulk. The yield is from 20 to 25% of the theoretical.

T. A. H.

Guaninepentoside from Molasses Residues. KARL ANDRLÍK (*7th Intern. Congr. Appl. Chem.* 1909, Sect. V., 331—337).—Molasses residues when boiled with copper sulphate and sodium hydroxide yield about 0·04% of guanine pentoside, $C_5H_8O_4,C_5H_5N_5O,2H_2O$, which crystallises in slender, colourless, sparingly soluble needles. When boiled with dilute mineral acids, it is hydrolysed to a pentose, $[\alpha]_D - 16{\cdot}7°$ (41·9%), and guanine (40%), and the pentoside becomes brown at 234—241°, m. p. (decomp.) above 300°; in dilute sulphuric acid it has $[\alpha]_D - 13{\cdot}95°$. E. F. A.

Nitropyrrole. ANGELO ANGELI and LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 311—314).—Pyrrole can be nitrated by the method previously suggested (*ibid.*, 1902, 11, ii, 16) using ethyl nitrate in the presence of sodium ethoxide or metallic sodium, and if the isolation of the sodium compound of nitropyrrole is avoided (for it was found to be spontaneously inflammable, *loc. cit.*), nitropyrrole can be prepared. Pyrrole diluted with ether is treated with sodium wire (1 mol.) and ethyl nitrate (1 mol.); the reaction is commenced by

slightly warming, and, after some days at the ordinary temperature (protected from moisture and carbon dioxide), the sodium will have disappeared. Ice is then added, and from the mixture of nitrite and *sodium* salt obtained, the former is removed by taking advantage of the insolubility of the *silver* salt of nitropyrrole. The sodium salt is then again obtained, and from it by the action of carbon dioxide free *nitropyrrole* is prepared. It forms pale yellow, glistening scales or prisms, or rhombohedra, m. p. 63·5°. Of the two possible constitutions, that of 3-nitropyrrole is considered the more probable.

Nitro-2 : 4-*dimethylpyrrole*, of the probable formula

$$\begin{array}{l}C(NO_2){:}CMe \\ | \\ CMe{=\!=}CH\end{array}\!\!>\!NH,$$

is prepared similarly, but more easily, because the slighter solubility of its *sodium* compound renders purification by means of the silver compound unnecessary. It crystallises in prisms, m. p. 111°. Both these nitro-compounds are unaffected by permanganate in alcoholic solution. R. V. S.

Action of Cyanacetic Ester on *o*- and *p*-Hydroxybenzaldehydes in the Presence of Ammonia. Mario Sclavi (*Atti R. Accad. Sci. Torino*, 1911, 46, 181—194).—By the interaction of *p*-hydroxybenzaldehyde (1 mol.) with cyanoacetic ester (2 mols.) and ammonia (3 mols.) at the ordinary temperature, the author has obtained the ammonium salt of *p*-hydroxybenzaldicyanoglutaconimide [2 : 6-diketo-3 : 5-dicyano-4-*p*-hydroxyphenyltetrahydropyridine],

$$HO{\cdot}C_6H_4{\cdot}C\!\!<\!\!\begin{array}{l}C(CN)\!-\!\!-CO\\CH(CN){\cdot}CO\end{array}\!\!>\!N{\cdot}NH_4,2H_2O,$$

and as secondary products the two corresponding (saturated and unsaturated) amides. From salicylaldehyde, *o*-hydroxybenzylidenedicyanodiacetic ester was chiefly formed, along with an *ammonium* salt which could not be identified.

The *ammonium* salt of 2 : 6-diketo-3 : 5-dicyano-4-*p*-hydroxyphenyltetrahydropyridine is a white substance, which does not melt below 300°, and does not lose ammonia even at 100°. By double decomposition in aqueous solution a number of crystalline salts were prepared from it, including those of iron (*ferric* and *ferrous*), *copper*, and *potassium*. The last is sparingly soluble in the cold, solutions containing only one part in three thousand of potassium chloride being precipitated after some hours. The *magnesium* salt,

$$(C_{13}H_6O_3N_3)_2Mg,6H_2O,$$

forms long, colourless crystals. The *barium* salt,

$$(C_{13}H_6O_3N_3)_2Ba,6H_2O,$$

crystallises similarly. The *silver* salt, $C_{13}H_6O_3N_3Ag,H_2O$, forms yellowish-white crystals, which change in the light. 2 : 6-*Diketo*-3 : 5-*dicyano*-4-p-*hydroxyphenyltetrahydropyridine*, $C_{13}H_7O_3N_3$, obtained from the barium or silver salt, forms lustrous, white crystals. α-*Cyano*-p-*hydroxyphenylacrylamide*, $OH{\cdot}C_6H_4{\cdot}CH{:}C(CN){\cdot}CO{\cdot}NH_2$, forms bright yellow crystals, m. p. 245° (with evolution of ammonia). α-*Cyano*-β-p-*hydroxyphenylpropionamide*,

$$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CN){\cdot}CO{\cdot}NH_2,$$

forms long, colourless crystals, m. p. 156°. R. V. S.

Rupture of the Pyridine Ring. WILHELM KÖNIG and R. BAYER (*J. pr. Chem.*, 1911, [ii], **83**, 325—328).—In this preliminary note the authors mention a number of substances, inorganic and organic, the additive compounds of which with pyridine are decomposed by primary or secondary amines, preferably aniline or 2-methyldihydroindole, yielding, by rupture of the pyridine ring, the so-called "pyridine dyes" (compare Reitzenstein and Breuning, this vol., i, 225).

C. S.

The New Series of Leuco-bases and Colouring Matters from Diphenylethylene. PAUL LEMOULT (*Compt. rend.*, 1911, **152**, 962—964. Compare Abstr., 1909, i, 836; Busignies, Abstr., 1909, i, 736).—Wahl and Meyer (Abstr., 1910, i, 134) having called in question the author's view that the presence of hydrogen attached to the ethylenic carbon atom in alkyl derivatives of di-*p*-aminodiphenylethylene is essential for the production of blue dyes from these leuco-bases, a further series of the compounds has been examined.

Michler's ketone was treated with a magnesium alkyl iodide, using the methyl, ethyl, *n*-propyl, *iso*propyl, *n*-butyl, *n*-sec.-butyl, *iso*amyl, and *cyclo*hexyl compounds. Two series of derivatives were thus obtained: compounds of the type $CHR\colon C(C_6H_4\cdot NMe_2)_2$, giving intense green or blue colorations with nitrous acid, and compounds of the type $CRR'\colon C(C_6H_4\cdot NMe_2)_2$, which gave extremely pale colorations when oxidised in this way. Corresponding colours were obtained on satinette mordanted with tannin.

n-*Propylidenetetramethyldiaminodiphenylmethane*,

$$CHEt\colon C(C_6H_4\cdot NMe_2)_2,$$

has m. p. 47·5°; the iso*propylidene* compound, m. p. 89°; the corresponding n-*butylidene* compound, m. p. 50·5°; the n-sec.-*butylidene* derivative, $CMeEt\colon C(C_6H_4\cdot NMe_2)_2$, m. p. 79°.

W. O. W.

Tautomerism of Amidines. RUDOLF PUMMERER (*Ber.*, 1911, **44**, 810. Compare this vol., i, 231).—O. Fischer (Abstr., 1907, i, 353) has already shown that Meldola's amidines derived from naphthalene (Trans., 1903, **83**, 1185) are not tautomerides. J. J. S.

Compounds of Antipyrine with the Chlorides of Tin. CHARLES ASTRE and J. VIDAL (*Bull. Soc. chim.*, 1911, [iv], **9**, 309—312. Compare Abstr., 1900, i, 362—411).—When a solution of 10 grams of stannous chloride in 100 c.c. of concentrated hydrochloric acid diluted with its own volume of water is added drop by drop to a solution of 10 grams of antipyrine in 100 c.c. of the same acid, a white precipitate is obtained having the composition

$$4C_{11}H_{12}ON_2,SnCl_4,4HCl.$$

This precipitate is not formed at 100°, but, on cooling the solution, the compound separates in large, tabular, clinorhombic crystals, which can also be obtained by immersing strips of tin in a hydrochloric acid solution of antipyrine. The crystals become pasty at 80°, but the melting point is not definite. The change from stannous to stannic chloride in the presence of antipyrine is not an isolated fact, since ferrous chloride is similarly oxidised to ferric chloride.

When the stannous chloride is replaced by stannic chloride, microscopic, white, clinorhombic crystals are obtained, having the composition: $3C_{11}H_{12}ON_2,SnCl_4,3HCl$, which also possess no definite melting point. They can be distinguished from the former compound by the fact that their solution in hydrochloric acid does not give precipitates with solutions of mercuric chloride and potassium ferricyanide. With the former compound the precipitates are white and green in colour respectively. T. S. P.

Action of ydrazine Hydrate on Ethyl Chloroacetate. THEODOR CURTIUS and LUDWIG HUSSONG (*J. pr. Chem.*, 1911, [ii], 83, 249—278).—The authors mention the complex reactions by which hydrazino-fatty acids have been prepared, and also refer to the unsuccessful attempts of Schöfer (*Diss.*, Kiel, 1892) and of Foersterling (Abstr., 1895, i, 3 4) to obtain hydrazinoacetic acid by the action of hydrazine hydrate and phthalylhydrazide respectively on ethyl chloroacetate. They find at the addition of ethyl chloroacetate to hydrazine hydrate results in the formation chiefly of hydrazinoacethydrazide, whilst by reversing the order of the addition hydrazinodiacethydrazide is the main product; in both cases, however, about 50% of the ester is reduced to ethyl acetate, an equivalent amount of nitrogen being evolved.

For example, ethyl chloroacetate is added slowly to hydrazine hydrate below 70° (the nitrogen evolved is collected and measured), and the product is diluted with water and shaken for a long time with successive small quantities of benzaldehyde. The resulting benzylidene compounds (except that which is obviously pure benzaldazine) are treated successively with 95% alcohol, light petroleum, and benzene. The residue obtained by evaporating the last solution is purified by alcohol, whereby *tribenzylidenehydrazinoacethydrazide* (annexed formula), m. p. 176° (decomp.), is obtained in white needles. This

$$\begin{array}{l} CH_2\cdot N\cdot N{:}CHPh \\ \mid \qquad > CHPh \\ CO{-}N\cdot N{:}CHPh \end{array}$$

substance, like tribenzylidenehydrazinodiacethydrazide (see below), dissolves in concentrated hydrochloric acid at 60°, but is not reprecipitated by dilution; by treating the diluted solution with sodium acetate, *dibenzylidenehydrazinoacethydrazide*,

$$CHPh{:}N\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot N{:}CHPh,$$

m. p. 161° (decomp.), is obtained. By prolonged boiling with hydrochloric acid, tribenzylidenehydrazinoacethydrazide is decomposed completely into its constituents.

Conversely, when hydrazine hydrate (3 mols.) is added to ethyl chloroacetate, and the product diluted with water and shaken repeatedly with benzaldehyde, the characteristic benzylidene compound obtained is *tribenzylidenehydrazinodiacethydrazide*,

$$CHPh{:}N\cdot N(CH_2\cdot CO\cdot NH\cdot N{:}CHPh)_2,$$

m. p. 219° (decomp.), in 15—20% yield. The substance dissolves in concentrated hydrochloric acid at 35—40°, and is recovered for the most part by diluting the solution with water; by keeping the undiluted solution at the ordinary temperature in contact with benzene, *hydrazinodiacethydrazide hydrochloride*,

$$NH_2\cdot N(CH_2\cdot CO\cdot NH\cdot NH_2)_2,3HCl,H_2O,$$

separates in yellowish-white crystals, which darken at 150°, and become greyish-black at 180°, without melting. By shaking a slightly acidified aqueous solution of the hydrochloride with benzaldehyde, hydrated tribenzylidenehydrazinodiacethydrazide, $C_{25}H_{24}O_2N_6,H_2O$, is obtained as a white powder, which sinters at 92°, partly melts at about 120°, and is fused completely at 190°; by treatment with absolute alcohol, the hydrated compound is converted into the anhydrous form mentioned above. In a similar manner, hydrazinodiacethydrazide hydrochloride can be converted into hydrated *tri*-m-*nitrobenzylidenehydrazinodiacethydrazide*, $C_{25}H_{21}O_8N_9,H_2O$, m. p. 222—223° (decomp.), and *tri*-m-*chlorobenzylidenehydrazinodiacethydrazide*, $C_{25}H_{21}O_2N_6Cl_3,H_2O$, which sinters at 100°, and melts between 110—180°; neither of these two compounds loses H_2O by boiling with alcohol or by prolonged heating at 60—70°.

Hydrazinodiacetic acid, $NH_2{\cdot}N(CH_2{\cdot}CO_2H)_2$, m. p. 166—167° (decomp.), is obtained by keeping tribenzylidenehydrazinodiacethydrazide in contact with concentrated hydrochloric acid and benzene for fifteen to twenty hours, separating the benzene layer, and distilling the acid solution with steam for twenty to twenty-five minutes. The acid is more conveniently obtained by adding hydrazine hydrate (about 5 mols.) to an alcoholic solution of chloroacetic acid, whereby nitrogen is not evolved, and a syrup is obtained which is diluted with water and shaken with benzaldehyde; the hydrazinodiacetic acid, which does not react with benzaldehyde, is thus obtained mixed with benzaldazine, and the two substances are easily separated by dissolving the latter in hot alcohol. From its method of formation, hydrazinodiacetic acid might have the symmetrical constitution

$$CO_2H{\cdot}CH_2{\cdot}NH{\cdot}NH{\cdot}CH_2{\cdot}CO_2H,$$

but this is rejected, because, although the acid itself does not react with benzaldehyde, its hydrazide does, yielding the tribenzylidenehydrazinodiacethydrazide described above. Moreover, the ease with which hydrazinodiacetic acid reduces ammoniacal silver solutions in the cold, Fehling's solution at the ordinary temperature, and mercuric oxide and potassium permanganate by warming, indicates the presence of the group $NH_2{\cdot}N{:}$ rather than ${\cdot}NH{\cdot}NH{\cdot}$. Ammonia, not hydrazine, is obtained when hydrazinodiacetic acid is heated with concentrated hydrochloric or sulphuric acid; the other product of hydrolysis could not be isolated.

By the action of hydrazine hydrate on ethyl bromoacetate, ethyl iodoacetate, ethyl di-iodoacetate, chloroacetamide, or di-iodoacetamide (all of which are prepared from ethyl diazoacetate), nitrogen is evolved, and the whole of the halogen is obtained in an ionic condition.

C. S.

Action of Hydrazine Hydrate on Ethyl Bromosuccinate. Theodor Curtius and Heinrich Gockel (*J. pr. Chem.*, 1911, [ii], 83, 279—311. Compare preceding abstract).—When hydrazine hydrate (4—5 mols.) is added to ethyl bromosuccinate and the mixture is heated for eight and a-half hours, the product is not a derivative of hydrazinosuccinic acid, but a mixture of 5-pyrazolone-3-carboxylohydrazide and its hydrazine salt; the same substance is obtained more

conveniently by von Rothenburg's method (Abstr., 1895, i, 302). The substance, which contains $\frac{3}{4}H_2O$, and has m. p. 253—254°, not 238—239°, forms a yellow *dihydrochloride*, $C_4H_6O_2N_4,2HCl$, which easily changes to a white *hydrochloride*, $C_4H_6O_2N_4,HCl$, and a *hydrazine* salt, $C_4H_6O_2N_4,N_2H_4$, m. p. 199—200° (decomp.). When heated with concentrated hydrochloric acid it yields 5-pyrazolone-3-carboxylic acid, which is converted by alcoholic hydrogen chloride into its ethyl ester and by nitrous acid into 4-oximino-5-pyrazolone-3-carboxylic acid; these compounds have been described by von Rothenburg (*loc. cit.*) and Ruhemann (Trans., 1896, 69, 1395).

5-Pyrazolone-3-carboxylohydrazide reacts with benzaldehyde in very dilute hydrochloric acid to form the *benzylidene* derivative, $C_{11}H_{10}O_2N_4$, m. p. 252—253° (decomp.), with ethyl acetoacetate to form the substance, $\begin{matrix}NH\text{—}N \\ | \\ CO\cdot CH_2\end{matrix}\!\!>\!C\cdot CO\cdot NH\cdot N\colon CMe\cdot CH_2\cdot CO_2Et$, m. p. 182° (decomp.), and with alcoholic benzoyl chloride ($1\frac{1}{2}$ mols.) in alkaline solution to form *4-benzoyl-5-pyrazolone-3-carboxylobenzoylhydrazide*,

$$\begin{matrix}NH\text{——}N \\ | \\ CO\cdot CHBz\end{matrix}\!\!>\!C\cdot CO\cdot NH\cdot NHBz,$$

m. p. 214° (decomp.), and *5-pyrazolone-3-carboxylobenzoylhydrazide*,

$$\begin{matrix}NH\text{—}N \\ | \\ CO\cdot CH_2\end{matrix}\!\!>\!C\cdot CO\cdot NH\cdot NHBz,$$

m. p. 269° (decomp.), the former being insoluble, the latter soluble, in sodium hydroxide.

4-Oximino-5-pyrazolone-3-carboxyloazoimide, $NH\!<\!\begin{matrix}CO\cdot C\colon NOH \\ | \\ N{=}C\cdot CO\cdot N_3\end{matrix}$, obtained by the action of sodium nitrite ($2\frac{1}{2}$ mols.) on 5-pyrazolone-3-carboxylohydrazide in dilute hydrochloric acid cooled by a freezing mixture, explodes at 100—105°. Its yellow ethereal solution reacts with ammonia, forming a flesh-coloured *ammonium* salt of 4-oximino-5-pyrazolone-3-carboxylamide, $NH\!<\!\begin{matrix}CO\cdot C\colon NO\cdot NH_4 \\ | \\ N{=}C\cdot CO\cdot NH_2\end{matrix}$, darkening at 220—290°, an alkaline solution of which, by acidification, yields *4-oximino-5-pyrazolone-3-carboxylamide*, a greenish-yellow powder darkening at 240°. The ethereal solution of the azoimide reacts with aniline to form a mixture of the *anilide*, $NH\!<\!\begin{matrix}CO\cdot C\colon NOH \\ | \\ N{=}C\cdot CO\cdot NHPh\end{matrix}$, m. p. 211—216° (decomp.), and its *aniline* salt, $C_{10}H_8O_3N_4,PhNH_2$ (which exists in two forms: yellow, m. p. 161—164°, and red, m. p. 158—162°), and with p-toluidine yielding the p-*toluidide*, $C_{11}H_{10}O_3N_4$, m. p. 222—223° (decomp.), and its p-*toluidine* salt.

Methyl 4-oximino-5-pyrazolone-3-carbamate, $NH\!<\!\begin{matrix}CO\cdot C\colon NOH \\ | \\ N{=}C\cdot NH\cdot CO_2Me\end{matrix}$, m. p. 218° (decomp.), is obtained by boiling the pure dry azoimide with an excess of methyl alcohol, and separates from methyl alcohol in small, red needles containing $\frac{3}{4}$MeOH. The corresponding *ethyl* ester, prepared in a similar manner, has m. p. 174° (decomp.), and also separates from methyl alcohol in red needles containing $\frac{3}{4}$MeOH. The methyl ester is decomposed by boiling 20% hydrochloric acid,

yielding carbon dioxide, hydrogen cyanide, hydrazine, hydroxylamine, ammonia, oxalic acid, and a yellow substance, $C_3H_3O_2N_3$, which darkens on heating, but does not melt below 300°, dissolves easily in sodium hydroxide or carbonate, develops a dark red coloration with ferric chloride, and does not react with benzaldehyde or phenylhydrazine; possibly it is *bis*-4-*oximino*-5-*pyrazolidone*,

$$\begin{matrix} NH\text{——}NH \\ | \qquad\qquad \\ CO\cdot C(NOH) \end{matrix}\!\!>\!C{:}C\!<\!\!\begin{matrix} NH\text{——}NH \\ \qquad\qquad | \\ C(N\cdot OH)\cdot CO \end{matrix}.$$

C. S.

Decomposition of Uric Acid by Organic Alkaline Solvents. HANNAH STEVENS and CLARENCE B. MAY (*J. Amer. Chem. Soc.*, 1911, **33**, 434—447).—It is well known that uric acid is decomposed by solutions of alkali hydroxides and carbonates. Experiments have now been made to ascertain the behaviour of uric acid in solutions of certain organic bases, namely, piperazine, urotropine, and lycetol (piperazine tartrate). The action of piperazine is of special interest, since this substance is used medicinally as a uric acid solvent.

Uric acid dissolves readily in piperazine at the ordinary temperature, but only slightly in urotropine, lycetol, or ammonium hydroxide. Piperazine, ammonium sulphide, and ammonium hydroxide effect the decomposition of uric acid in the absence of neutral salts, but the decomposition by piperazine takes place more slowly in presence of ammonium sulphate, disodium hydrogen phosphate, or sodium chloride. Urotropine exerts but little action on uric acid.

When uric acid is boiled with ammonium sulphide solution, it is decomposed to almost the same extent as it is by sodium sulphide solution, but thiouranil does not seem to be produced. E. G.

Quadriurates. OTTO ROSENHEIM (*Zeitsch. physiol. Chem.*, 1911, **71**, 272).—The conclusion arrived at by Kohler (this vol., i, 243) that quadriurates are mixtures of biurates and uric acid was reached experimentally by the author in conjunction with Tunnicliffe some years ago (*Lancet*, June 16th, 1900). W. D. H.

Recovery of Adenine. GEORGE DE F. BARNETT and WALTER JONES (*J. Biol. Chem.*, 1911, **9**, 93—96).—To free adenine from hypoxanthine, the base must be converted into the picrate, which as such is useless, and can be changed into a non-toxic salt only by the use of an excessive amount of ether. When, however, the picrate is dissolved in ammonia and the solution treated with ammoniacal silver nitrate, the adenine is precipitated quantitatively, whilst more than 90% of the picric acid remains dissolved. This forms the basis of a method of recovering adenine and of dealing with filtrates from adenine picrate, which contain other purine bases as well as picric acid. W. D. H.

Conversion of Arylamineazo*iso*oxazolones into Azopyrazolones. CARL BÜLOW and ARNULF HECKING (*Ber.*, 1911, **44**, 467—480).—A third method of preparing pyrazolone dyes is based on the observation of Knorr and Reuter (Abstr., 1894, i, 372), that by the action of phenylhydrazine on the phenylhydrazone of ketomethyl-

*iso*oxazolone in acetic acid solution the phenylhydrazine of ketophenylmethylpyrazolone is obtained. This method is now extended to a number of substituted *iso*oxazoles (Bülow and Hecking, this vol., i, 244), both hydrazine, phenylhydrazine, and dinitrophenylhydrazine being used. The conversion depends on the strength of the base used, and is a function of the solubility of the reaction product.

The azopyrazolones possess all the tinctorial properties of the true *o*-hydroxyazo-dyes, in particular the fastness to alkali. Their properties also depend on the nature of the arylamine azo-residue, and on the group attached to the nitrogen of the heterocyclic ring,

$$R'N<\begin{matrix}C(OH){:}CN{:}NR \\ N\!=\!=\!=\!=CMe\end{matrix}.$$

When R is a purely aromatic radicle and R′ is hydrogen, the acidity of the compound increases, and it dissolves easily in a very small quantity of piperidine. It is not precipitated from the solution by the continued addition of water; the yellow colour is not altered by the addition of alkali hydroxide. The dissolved salt is decomposed, however, by carbon dioxide.

When R′ is a purely aromatic radicle, the compound also readily dissolves in piperidine, but the salt is hydrolysed on the addition of a certain quantity of water. The very finely-divided precipitate dissolves again in alkali hydroxide.

The solutions of the monoazopyrazolone dyes in concentrated sulphuric acid are yellow so long as only benzene residues are present. Derivatives of α-naphthylamine are deep bluish-red or reddish-violet; those of β-naphthylamine are brownish-red.

4-Benzeneazo-5-hydroxy-3-methylpyrazole, prepared from the corresponding *iso*oxazole and hydrazine hydrate, forms reddish-yellow platelets, m. p. 199°.

4-p-*Nitrobenzeneazo-5-hydroxy-3-methylpyrazole* crystallises in slender, yellow needles, m. p. 264—265°. It behaves towards potassium hydroxide as a very weak dibasic acid; in dilute alkali it dissolves with a brown colour; in 50% alkali this changes to bluish-red, and after a time reddish-violet needles separate; on dilution the bluish-red solution becomes brown again. Carbon dioxide precipitates the unaltered azo-dye. Many of the other azopyrazoles described behave similarly.

4-p-*Nitrobenzeneazo-5-hydroxy-*1-*phenyl-*3-*methylpyrazole* forms red needles, m. p. 198°; the phenolic *potassium* salt crystallises in slender, matted, brown needles.

4-op-*Dinitrobenzeneazo-*5-*hydroxy*-3-*methylpyrazole* crystallises in yellowish-red, flat needles, m. p. 277—278°. The *di*(?)*potassium* salt separates in brownish-blue flakes.

4-op-*Dinitrobenzeneazo-*5-*hydroxy-*1-*phenyl-*3-*methylpyrazole* is obtained in violet-red needles, m. p. above 300°.

4-*Benzeneazo-5-hydroxy-*1-op-*dinitrophenyl-*3-*methylpyrazole* crystallises in short, thick, dirty violet needles, m. p. 216—217°.

4-o-*Tolueneazo-5-hydroxy-3-methylpyrazole* separates in rhombic aggregates of tiny, reddish-yellow plates, m. p. 221—223°. The isomeric 4-p-*Tolueneazo-5-hydroxy-3-methylpyrazole* is obtained in smaller yield; it crystallises in lustrous, orange needles, m. p. 195—196°. The two

isomerides show similar shades in the same solvent, the para-derivative being more soluble.

4-o-*Tolueneazo-5-hydroxy-1-phenyl-3-methylpyrazole* crystallises in yellowish-red needles, m. p. 181—182°. The same compound is obtained by the combination of 1-phenyl-3-methyl-5-pyrazolone with the diazo-compound of *o*-toluidine (D.R.-P. 153861). The isomeric 4-*p*-tolueneazo-5-hydroxy-1-phenyl-3-methylpyrazole separates in red needles, m. p. 137° (compare Lapworth, Trans., 1903, 83, 1124).

4-m-*Xyleneazo-5-hydroxy-4-methylpyrazole* forms very slender, matted, silky, glistening, orange needles, m. p. 190—191°.

4-m-*Xyleneazo-5-hydroxy-1-phenyl-3-methylpyrazole* is obtained in aggregates of lustrous, yellowish-red, rhombic plates, or slender, orange needles, m. p. 167°.

4-*α-Naphthaleneazo-5-hydroxy-3-methylpyrazole* separates in orange-red plates, m. p. 247°. The corresponding 4-*α-naphthaleneazo-5-hydroxy-1-phenyl-3-methylpyrazole* crystallises in lustrous, yellowish-red needles, m. p. 202—203°.

4-*β-Naphthaleneazo-5-hydroxy-3-methylpyrazole* is a bright red, crystalline powder, m. p. 238—239°. 4-*β-Naphthaleneazo-5-hydroxy-1-phenyl-3-methylpyrazole* forms short needles, m. p. 186—187°. The yellow solution in piperidine becomes milky when considerably diluted.

4-o-*Carboxybenzeneazo-5-hydroxy-3-methylpyrazolone*, prepared by boiling hydrazine hydrate with the oxime of ethyl *o*-carboxybenzeneazo-acetoacetate, forms microscopic aggregates of brownish-yellow plates, m. p. 280°.

4-o-*Carboxybenzeneazo-5-hydroxy-1-phenyl-3-methylpyrazole* crystallises in very beautiful orange-red, stunted needles with a blue surface reflex, m. p. 269—270°.

4-*Nitro*-o-*carboxybenzeneazo-5-hydroxy-1-phenyl-3-methylpyrazole* separates in reddish-violet needles with a lustrous, blue reflex, m. p. 285°.

E. F. A.

The Heat Coagulation of Proteins. I. Is the Hydrogen Ion Concentration Altered on Coagulation? SÖREN P. L. SÖRENSEN and E. JÜRGENSEN (*Biochem. Zeitsch.*, 1911, 31, 397—442).—The authors in an extensive series of experiments with different acids have determined the optimal conditions of coagulation, generally by estimating the amount of nitrogen in the uncoagulated portion of the solution. In these experiments they have also made numerous measurements of the hydrogen ion concentration in the mixtures, both before and after coagulation by means of concentration cells. The optimal concentration for coagulation is about $p_H = 4{\cdot}6$, but varies slightly with the concentration of the protein (blood-serum or egg-white), and is somewhat lower than the isoelectric point, $p_H = 5{\cdot}52$, as determined by Michaelis and Rona. After coagulation the hydrogen ion concentration becomes smaller, and this the authors ascribe to the separation of the protein from solution, the protein itself having acidic functions, to which the hydrogen ion concentration of the solution are due. This explains the slight variability in the hydrogen ion concentration which affords the optimal conditions of coagulation in proteins of varying strengths of solution. (It is higher for

stronger than weaker solutions.) No carbon dioxide is evolved during coagulation. Certain peculiarities in the case of egg-white solutions were observed. The maximal separation under optimal conditions of the coagulum is in this case only reached after several hours, after which, owing to the action of the liquid, some of the coagulum passes again into solution. S. B. S.

The Fixing of Acids by Egg-albumin and Viscosity. WILHELM E. RINGER (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 243—260).—The nature of acid protein solutions has been investigated by measurements of the *E.M.F.* of hydrogen concentration cells, of electrical conductivity, and of viscosity. Solutions containing egg-albumin and variable amounts of hydrochloric acid or sodium hydroxide, and, in addition, solutions of egg-albumin, serum-albumin, and serum-globulin with varying amounts of acetic acid, were examined in detail. The results of these measurements indicate that considerable amounts of acid and alkali are fixed by the proteins, and the process is considered to be in the nature of chemical combination rather than adsorption. H. M. D.

Electrochemistry of Proteins. IV. Dissociation in Solutions of the Globulinates of the Alkaline Earths. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1911, 15, 166—177. Compare Abstr., 1910, ii, 679, 939; Hardy, Abstr., 1906, i, 121).—The conductivity at 30° of solutions of potassium, calcium, barium, and strontium hydroxides neutralised to phenolphthalein with globulin show that the salts obey Ostwald's dilution law. The same conclusion may be drawn for sodium globulinate at 18° from Hardy's measurements.

As in the case of the caseinogenates, the value of $\rho(v_1+v_2)$ is about twice as great for the alkalis as the alkaline earths, where v_1, v_2 are the ionic mobilities, and ρ the number of equivalents of salt formed from one equivalent of alkali.

It is assumed that ρ equals 2 for the alkali salts, so that (v_1+v_2) is about the same (26×10^{-5} cm. per sec.) for all the globulinates, a result in accord with Hardy's measurements of the velocity of the globulin ion.

At neutrality to phenolphthalein the globulinates dissociate into two protein ions, each possessed of twice as many valencies as there are molecules of base bound up in one molecule of globulinate. The simplest formula of potassium globulinate, $KX^{\cdot\cdot}+X(OH)_n{}''$, does not explain the fact that the alkali globulinates take up a second equivalent of globulin, becoming neutral to litmus. These are represented: $KHX^{\cdot\cdot\cdot\cdot}+X(OH)_n{}''''$, so that the salt neutral to phenolphthalein is $K_2X^{\cdot\cdot\cdot\cdot}+X(OH)_n{}''''$, and the corresponding alkaline earth salt, which is saturated with globulin, although neutral to phenolphthalein only, is represented: $Ca_2(X)_2{}^{\cdot\cdot\cdot\cdot}+X_2(OH)_{2n}{}''''$.

On this assumption the ions are quadrivalent, and the dissociation constants for the globulinates are: K, 0·01470; Ca, 0·00360; Ba, 0·00493; Sr, 0·00211. R. J. C.

Histidine in Pig's Thyreoglobulin. FRED C. KOCH (*J. Biol. Chem.*, 1911, 9, 121—122).—Nürnberg failed to obtain enough histidine from thyreoglobulin (from ox-thyroids) to definitely establish its presence. In the present research, sufficient was obtained for the purpose. The material was prepared from pig's thyroids.

W. D. H.

Swelling of Casein Under the Influence of Sodium Chloride and Lactic Acid. W. VAN DAM (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 102—107. Compare this vol., i, 91).—The structure of cheese is sometimes dough-like and sometimes granular, and the author has endeavoured to trace the cause of this difference by determining the amount of casein dissolved by solutions containing 5%, 3%, and 1% of sodium chloride and various amounts of lactic acid. Curves showing the relation between the dissolved casein and the concentration of the hydrogen ions are given. A. J. W.

Electrochemistry of Proteins. V. The Electrochemical Equivalent of Caseinogen and its Relation to the Combining and Molecular Weights of Caseinogen. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1911, 15, 178—196. Compare preceding page).—Electrolysis of potassium caseinogenate with a current of 0·001 ampere liberates gas at both electrodes, and on the anode a firm, white, spongy precipitate is deposited, the cellular texture of which is apparently due to gaseous oxygen. The deposit consists of normal caseinogen containing less than 0·2% of ash.

The amount of caseinogen removed from the solution was determined by the refractometer, and a correction was applied to the experimental data to compensate for loss of caseinogen from the anode by dissolution in the electrolyte, the amount of this correction depending on the alkalinity of the solution and the duration of electrolysis.

The electrochemical equivalent of caseinogen in solutions containing 50×10^{-5} to 100×10^{-5} equivalents of potassium hydroxide per gram is $0{\cdot}0242 \pm 0{\cdot}0019$ gram of caseinogen per coulomb as a mean of fourteen determinations. This must be the equivalent of caseinogen at its minimum, since, whatever the proportion of potassium hydroxide to caseinogen in the electrolyte, no caseinogen will be deposited until the potassium hydroxide in the anode film is saturated.

The equivalent of caseinogen is therefore 2336 ± 183 at saturation. Since 1 gram of caseinogen saturates $11{\cdot}4 \times 10^{-5}$ equivalents of potassium hydroxide, the molecular weight of caseinogen is $(8772)_n$, and the basicity, $(8772)_n \div (2336 \pm 183)$, that is, 4, or some multiple of 4.

The formula of potassium caseinogenate in solutions neutral to phenolphthalein was deduced from cryoscopic determinations to be $K_2X^{\cdot\cdot\cdot\cdot} + X(OH)_n^{''''}$, molecular weight 2200, admixed with a small proportion of $(KHX)_2^{\cdot\cdot\cdot\cdot} + X_2(OH)_{2n}^{''''}$, molecular weight 4400, the latter being the main constituent in solutions neutral to litmus. At saturation the formula is: $KH_7X_4^{\cdot\cdot\cdot\cdot} + X_4(OH)_{4n}^{''''}$, molecular weight 8800.

The conductivity of calcium hydroxide solution in presence of

caseinogen indicates that the alkalis and alkaline earths dissolve caseinogen in equivalent proportions. The author discusses the formula and dissociation of the alkaline-earth caseinogenates in view of the difference between caseinogen and globulin in this repect.

The percentage of glutamic acid in caseinogen indicates a minimum molecular weight of 1336 (4008/3), whereas the tyrosine indicates 4022. The sulphur and phosphorus also indicate a minimum molecular weight of about 4000. R. J. C.

Inosic Acid. IV. PHŒBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1911, 44, 746—753. Compare Abstr., 1908, i, 931; 1909, i, 164, 540).—The phosphoric acid residue in *d*-ribosephosphoric acid is attached to the δ-carbon atom of the ribose molecule, since, on oxidation with nitric acid ($D = 1 \cdot 2$) at 40° and subsequent rapid evaporation and treatment with calcium hydroxide, calcium phospho-ribonate and calcium phosphate are obtained. The calcium salt is identical with that obtained from the oxidation product of *d*-ribosephosphoric acid. By the hydrolysis of phospho-*d*-ribonic acid at 130° in neutral solution (ammonium acetate), *d*-ribonic acid is obtained, which is identical with the acid formed when *d*-ribose is oxidised with bromine water.

Details for the preparation of *d*-ribosephosphoric acid are given.
J. J. S.

Inosic Acid. WALTER A. JACOBS and PHŒBUS A. LEVENE (*Proc. Amer. Soc. Biol. Chem.*, 1910, xxv; *J. Biol. Chem.*, 9).—Inosic acid is hypoxanthine phosphoriboside. The phosphoric acid group is bound to the ω-carbon atom of the ribose. W. D. H.

Oxyprotosulphonic Acid. JÓZEF BURACZEWSKI and L. KRAUZE (*Zeitsch. physiol. Chem.*, 1911, 71, 153—156).—The oxyprotosulphonic acids (compare Maly, Abstr., 1885, 824) of egg-albumin, serum-albumin, and casein are differentiated on treatment with boiling glacial acetic acid into acid compounds (*a*) insoluble in acetic acid, termed α-oxyprotosulphonic acid, and (*b*) soluble in acetic acid, but precipitated by ether or by water, termed β-oxyprotosulphonic acid. On cooling the acetic acid solution, an acid substance separates in the case of egg- and serum-albumin, which has not been further investigated. The relation of carbon to nitrogen in both α- and β-oxyprotosulphonic acids indicates that the protein molecule has not been hydrolysed in their formation. E. F. A.

Some Physico-chemical Properties of Lecithin Emulsions and of Lecithin–Protein Mixtures. HANS HANDOVSKY and RICHARD WAGNER (*Biochem. Zeitsch.*, 1911, 31, 32—45).—Lecithin emulsions show an increased viscosity as compared with water, which is diminished on the addition of electrolytes. The lecithin precipitation by hydrochloric acid can be inhibited by salts in concentrations in which they themselves do not precipitate it. Indifferent narcotics have no effect on the viscosity. Globulin can be precipitated by lecithins from sera which are poor in electrolytes (that is, have just sufficient salts to hold the globulin in solution). The precipitation is

inhibited by neutral salts. Neither precipitation nor viscosity phenomena give any indication of a colloid complex between lecithin and neutral serum albumin when lecithin is added in the form of an emulsion. S. B. S.

The Valency of Iron in Blood Pigment. WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1911, 71, 100—104).—Polemical. Reasons are given why the author disagrees with Manchot's conclusion that the iron of hæmoglobin cannot be in ferrous, but must be in ferric combination. W. D. H.

The Theory of Enzyme Action. OSCAR LOEW (*Biochem. Zeitsch.*, 1911, **31**, 159—167).—The author claims that his views on enzyme action have been misrepresented in recent text-books on enzymes, in that it has been stated that the labile enzymatic substances decompose explosively. He distinguishes between two kinds of substances with chemical lability, the "potentially-labile," which on small stimulus decompose explosively, and the "kinetically-labile," where the energy is exerted in a continuously active form. The differences are illustrated by various examples. S. B. S.

Reversibility of Enzyme Action. ADOLF WELTER (*Zeitsch. angew. Chem.*, 1911, **24**, 385—387).—A brief résumé is given of the more important cases in which the reversibility of enzyme action has been demonstrated (compare Croft Hill, Trans., 1898, **73**, 634; Proc., 1901, **17**, 184; Kastle and Loevenhart, Abstr., 1901, i, 178; Visser, *ibid.*, 1905, ii, 577; Hanriot, *ibid.*, 1901, ii, 175; Pottevin, *ibid.*, 1903, ii, 494). Details are given for the production of fatty acids on the large scale by the hydrolysis of natural fats by means of the lipatic enzyme present in seeds. Experiments are also described which prove that in the absence of large quantities of water these enzymes are capable of synthesising appreciable amounts of esters from glycerol and the acids derived from certain natural fats. J. J. S.

Composition of Invertase. ALBERT P. MATHEWS and T. H. GLENN (*J. Biol. Chem.*, 1911, **9**, 29—56).—As ordinarily prepared, invertase is probably a combination of a protein and a mannosan. All attempts to free the protein from the gum and retain enzymic activity were failures. Acid alcohol destroys the activity. The parallelism between activity and nitrogen content is believed to indicate that the active substance is a protein. W. D. H.

Temperature-coefficient of the Decomposition of Invertase. HANS EULER and SIXTEN KULLBERG (*Zeitsch. physiol. Chem.*, 1911, 71, 134—142. Compare Euler and Ugglas, Abstr., 1910, i, 345, 796).—The influence of heating for half an hour at various temperatures on invertase prepared by autolysis has been determined. Half of the invertase is destroyed under these conditions at $63° \pm 0·2°$. In an extract of dried yeast the presence of proteins and carbohydrates has no influence on the heat stability of invertase. Lactose has no protective influence; phosphate has also no influence. There

is no difference in the heat stability of invertase from top and bottom fermentation yeasts, contrary to statements on this point in the text-books of Effront and Oppenheimer. E. F. A.

Nucleases. PHŒBUS A. LEVENE and FLORENTIN MEDIGRECEANU (*J. Biol. Chem.*, 1911, 9, 65—83).—Plasma of heart muscle, liver, kidney, and intestinal mucosa hydrolyse inosin, giving rise to the free base and *d*-ribose; plasma of pancreas and blood serum have no effect. Inosic acid is hydrolysed into phosphoric acid, *d*-ribose, and hypoxanthine by the same materials. The same plasmata hydrolyse guanylic acid, with the addition of that of the pancreas (one experiment); the tendency to gelatinise causes difficulties in the investigation of guanylic acid. Cytidin is regarded as a complex of pentose and cytosine, although not in glycosidic linking; no cleavage occurred with any plasma. The cleavage of yeast nucleic acid by the plasmata into phosphoric acid, purine bases, *d*-ribose, cytidin, and uridin was incomplete. No definite regularity in the velocity of the reactions was noticed. W. D. H.

Nucleases. WALTER JONES (*J. Biol. Chem.*, 1911, 9, 129—138). —A nuclease is generally understood to be an enzyme which liberates purine bases from nucleic acid in a form in which they are directly precipitable by the reagents usually employed for that purpose. The definition is, however, unsatisfactory. There is, further, no assurance that the enzyme of one gland can decompose the nucleic acid of another organ. The nucleic acids are constituted on one type; according to Levene and Jacobs, a phosphoric acid group is linked to a nitrogenous ring by *d*-ribose. This "nucleotide" structure is common to all nucleic acids, but differences occur in the nitrogenous rings and in re-duplication of molecules; it would therefore be surprising to find one enzyme which can decompose them all. The present investigation deals with guanylic acid, a mononucleotide, that is, a nucleic acid which yields only one purine base, guanine. Extract of ox-spleen readily effects its decomposition, giving rise to xanthine and uric acid by oxidation of the guanine. Pig's pancreas cannot do this, although it is rich in nuclease. W. D. H.

The Physiological Agents Concerned in Nuclein Fermentation, with Special Reference to Four Independent Deamidases. WALTER JONES (*J. Biol. Chem.*, 1911, 9, 169—180).—Although pig's pancreas will not liberate the purine base from guanylic acid, it nevertheless liberates phosphoric acid, and thus converts guanylic acid into guanosine. Extracts of pig's spleen and liver have the same action, and also liberate phosphoric acid from thymus-nucleic acid. The nucleosides (such as guanosine) which remain are compounds of *d*-ribose and the purine base; the amino-nucleosides, guanosine and adenosine, can further be converted into xanthosine and inosine (or hypoxanthosine), the corresponding hydroxy-compounds, as Levene and Jacobs showed. Such deamidations are quite analogous to those which occur when guanine and adenine are converted into xanthine and hypoxanthine respectively. Nevertheless,

the deamidation is accomplished by different enzymes; thus guanase and guanosine-deamidase are separate enzymes; one is present, for instance, in pig's liver and the other is not. Similarly, adenosine-deamidase and adenase are not identical enzymes. W. D. H.

Pancreatic Lipase. ANT. HAMSIK (*Zeitsch. physiol. Chem.*, 1911, 71, 238—251).—Previous authors have noticed that filtration of a glycerol extract of pancreas removes its lipoclastic action. In the present research it is shown that clear glycerol extracts can be prepared from the dried pancreas of the pig, and that these retain their fat-splitting properties after filtration through a Chamberland filter. Pancreatic lipase is reversible in its action, and synthesises fat from palmitic and stearic acids and glycerol. Neutral salts inhibit both fat-splitting and fat-synthesis, but soaps act favourably on both.

W. D. H.

Significance of Colloidal Manganese Oxide Solutions in Biochemical Oxidations. BOUWE SJOLLEMA (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 399—406. Compare Abstr., 1909, ii, 484, and Marck, *Diss.*, Heidelberg, 1907).—By agitating samples of quinol solution with Marck's manganese solution, some in presence of peroxydase from horse-radish (*Cochlearia armoracia*) and some without it, the author found that the oxidation of the quinol and its transformation into quinhydrone by the manganese peroxide is facilitated by the presence of the peroxydase. In the oxidation of quinol, a mixture of colloidal manganese peroxide and a peroxydase behaves like the system peroxydase + oxygenase, so that the manganese plays the part of oxygenase. A. J. W.

Relation of Hæmoglobin Derivatives and Peroxydases to Inorganic Catalysts. W. MADELUNG (*Zeitsch. physiol. Chem.*, 1911, 71, 204—237).—It is probable that the mechanism of the action of oxydases, peroxydases, and catalases rests on an inorganic basis. Such ferment action is to be expected in all cases where compounds are present which are able to exist in several stages of oxidation, which are capable of forming unstable molecular compounds with molecules of oxygen or hydrogen peroxide, and in which the higher oxides can be converted into the lower and vice versâ. It is shown in the case of the blood-colouring matter that complex iron compounds fulfil these conditions, and it is probable that the greater part, if not all, such ferments owe their activity to complex iron compounds.

When neutral aqueous solutions of benzidine are oxidised in presence of traces of a neutral mineral salt, benzidine-blue is precipitated in the form of microscopic matted needles. On separating the dye, and adding hydrochloric acid to it, brown flakes of the dichloroimide are formed, which dissolve in potassium iodide, liberating iodine. The free iodine is titrated with thiosulphate, and a convenient measure of the oxidising activity is obtained. The benzidine is used in 0·04% solution containing 1% of sodium chloride, a considerable excess being employed.

With blood the amount of oxidising action is proportional to the amount taken. Small quantities of mineral acids prevent the

formation of the blue, but the amount formed is doubled on the addition of sodium acetate to the acid, or on saturating the neutral solution with carbon dioxide. The optimum amount of sodium chloride necessary for precipitation of the blue is about 1%. The activity of blood is roughly proportional to the hæmoglobin present.

E. F. A.

New Method for the Preparation of a Catalase from Blood and its Properties. JULES WOLFF and ELOI DE STŒCKLIN (*Compt. rend.*, 1911, **152**, 729—731).—The following process gives a catalase free from hæmoglobin, and oxyhæmoglobin free from catalase. Unlike Senter's method (Abstr., 1903, ii, 661) it does not diminish the activity of the enzyme. The corpuscles of defibrinated blood are washed with physiological salt solution and removed by centrifugation. The paste of corpuscles is made up to the original volume of blood with distilled water, laked with ether, and the liquid decanted and filtered. The filtrate is kept for twenty hours at $-10°$, after the addition of one-fifth its volume of alcohol. Oxyhæmoglobin crystallises out, and a further crop separates on addition of more alcohol. The liquid is now covered with a layer of toluene 0·5 cm. deep, which, after some days, precipitates proteins with the last traces of oxyhæmoglobin. The clear, yellow filtrate contains a stable and very active catalase.

It has been shown that pure oxyhæmoglobin is decomposed by hydrogen peroxide, whereas this is without action on the crude product. In the latter case the catalase present exerts a protective influence on the oxyhæmoglobin by facilitating the combination of oxyhæmoglobin with molecular oxygen.

W. O. W.

The Reduction Ferments. I. The Schardinger Enzyme (Perhydridase). ALEXIS BACH (*Biochem. Zeitsch.*, 1911, **31**, 443—449).—The enzyme acts in the system ferment–methylene blue–aldehyde–water. According to the author's theory, scission of water by the oxidisable substance (aldehyde) takes place under the influence of the catalyst, which forms with the hydrogen of the water a strongly reducing substance. He draws attention to the analogy of the reducing enzymes (for which he suggests the name reducase instead of the etymologically incorrect reductase) with the oxydases and peroxydases.

The Schardinger enzyme (that is, the enzyme acting in the methylene blue–aldehyde system) can be prepared from calf's liver by extracting the organ with 1% sodium hydrogen carbonate solution and neutralising the extract with acetic acid. From this extract the enzyme can be precipitated by alcohol, and from the precipitate it can be re-extracted in purer form by ½% sodium hydrogen carbonate, which extract acts readily after neutralisation with acetic acid.

S. B. S.

Organic Chemistry.

Preparation of Methyl Bromide. ARTUR BYGDÉN (*J. pr. Chem.*, 1911, [ii], 83, 421—424).—Methyl bromide is obtained in 83—84% yield (as against 44·5% by the bromine and phosphorus method) by adding carefully 450 grams of methyl alcohol to 600 grams of concentrated sulphuric acid, adding gradually 230 grams of water and 300 grams of powdered potassium bromide to the cold mixture, and heating until gas ceases to be evolved.

In some cases methyl bromide is a more suitable substance than methyl iodide for the preparation of the magnesium methyl halides; the gas in slight excess is passed into the mixture of ether and magnesium. C. S.

Equilibrium between *iso*Butyl and *tert.*-Butyl Bromides at Elevated Temperatures. ROGER F. BRUNEL (*Ber.*, 1911, 44, 1000—1009).—*iso*Butyl bromide usually contains traces of *n*-propyl bromide; attempts to purify *iso*butyl alcohol by means of the urethane were not successful, and finally very careful fractional distillation was resorted to for the preparation of the pure alcohol. This has b. p. 107·19—107·43°/760 mm., D_{25}^{25} 0·8002—0·80032, D_{4}^{25} 0·7979—0·79802, and gives *iso*butyl bromide, b. p. 91·1—91·5°, D_{25}^{25} 1·2624—1·2616, D_{4}^{25} 1·2588—1·2580.

Estimation of the *tert.*-butyl bromide present after heating either the *iso*- or *tert.*-butyl bromide at 280° until equilibrium is attained indicates the presence of 90·7% of the tertiary derivative in the equilibrated mixture. E. F. A.

Aliphatic Halogen Compounds from α-Pipecoline. JULIUS VON BRAUN and W. SOBECKI (*Ber.*, 1911, 44, 1039—1048).—By the action of phosphorus pentachloride on benzoyl-α-pipecoline the ring is opened and αε-dichlorohexane formed. With phosphorus pentabromide the chief product is αε-dibromohexane; in addition, an unsaturated bromide and considerable quantities of a *tribromide*, $C_6H_{11}Br_3$, are formed. This is due to part of the dibromohexane losing hydrogen bromide and forming an unsaturated compound of the constitution $CH_2Br\cdot[CH_2]_2\cdot CH{:}CHMe$ or $CH_2Br\cdot[CH_2]_2\cdot CH_2\cdot CH{:}CH_2$, which is immediately brominated by the phosphorus pentabromide at the double bond. The structure of the tribromide was determined by treatment with magnesium in ethereal solution, when either

$$MgBr\cdot[CH_2]_3\cdot CH{:}CHMe$$

or $MgBr\cdot[CH_2]_3\cdot CH_2\cdot CH{:}CH_2$ is formed. The action of carbon dioxide causes the formation of an unsaturated acid, $C_6H_{11}\cdot CO_2H$, which yields glutaric and acetic acids on oxidation, and therefore has the composition of a δε-heptenoic acid, $CO_2H\cdot[CH_2]_3\cdot CH{:}CH\cdot CH_3$.

The tribromide is accordingly αδε-tribromohexane. These products are all optically inactive.

$\alpha\epsilon$-Dibromohexane is a liquid of aromatic odour, b. p. 101—105°/ 9 mm., D_4^{20} 1·5989. Proof that the product does not contain also $\alpha\delta$-dibromohexane is afforded by the conversion into pure 1-benzyl-2-pipecoline by boiling with benzylamine in alcoholic solution. With aniline in a similar manner 1-phenyl-2-pipecoline is obtained; this is colourless, and has an agreeable odour resembling phenylpiperidine, b. p. 143°/20 mm. The picrate has m. p. 162°; the methiodide is a colourless, crystalline powder, m. p. 145°.

$\alpha\delta\epsilon$-*Tribromohexane* is a heavy, colourless liquid, b. p. 152—154°/ 16 mm, D_4^{20} 1·9613. $\Delta\delta$-Heptenoic acid (compare Fichter and Gully, Abstr., 1897, i, 590) has b. p. 117°/11 mm., D_4^{20} 0·9496, n_D 1·4444.

F. F. A.

Chloroacetylene. José Rodriguez Mourelo and A. García Banús (*Anal. Fis. Quim.*, 1911, **9**, 84—87).—Chloroacetylene may be prepared by the action of alcoholic sodium hydroxide on acetylene dichloride at 40° in a current of nitrogen, the operation being suitable for lecture demonstration.

G. D. L.

Fusibility Curves of Gaseous Mixtures; Compounds of Hydrogen Chloride and of Sulphur Dioxide with Methyl Alcohol. Georges Baume and Georges Pamfil (*Compt. rend.*, 1911, **152**, 1095—1097. Compare Abstr., 1909, ii, 545; 1910, ii, 825).—Vitrification at low temperatures prevents complete examination of the freezing-point curve for mixtures of methyl alcohol and hydrogen chloride. It has been followed, however, for mixtures containing 0—10, 35—55, and 90—100% of the alcohol, and shows a sharply defined maximum corresponding with a compound MeOH,HCl. Mixtures of methyl alcohol and sulphur dioxide are very viscous at low temperatures; the curve reveals the existence of two compounds, $MeOH,SO_2$ and $2MeOH,SO_2$. The system $HCl + SO_2$ shows a single eutectic and no maximum.

W. O. W.

Certain Properties of Aqueous Solutions of Trimethylcarbinol. Antony G. Doroschewsky (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 66—73).—From the values obtained by previous investigators and by himself, the author deduces the following constants for trimethylcarbinol: m. p. 25—25·5°, b. p. 82·55°, D_4^{25} 0·7806.

Examination of the values of D_4^{20} and of D_4^{25} obtained by Young and Fortey (Trans., 1902, **81**, 717) for various aqueous solutions of trimethylcarbinol shows that the rate at which the sp. gr. varies with the composition (ds/dp) changes irregularly at both temperatures, so that the fourth decimal figures of the values given are probably inaccurate.

A corrected table is given, showing for solutions containing from 0 to 100% of trimethylcarbinol the values of D_4^{25}, D_4^{20}, ds/dp at each of these temperatures, and ds/dt. The extent of the contraction occurring on mixing water and trimethylcarbinol increases with rise of temperature for concentrated solutions, and diminishes for solutions containing less than 70% of the alcohol. With rise of temperature, the maximum of contraction moves appreciably in the direction of the more concen-

trated solutions. With aqueous solutions of ethyl alcohol a totally different behaviour is observed; increases of the amount of contraction with temperature occurs with dilute solutions (10%), and the position of the contraction does not change even at very high temperatures.

For pure trimethylcarbinol, the author finds n_D^{25} 1·38548. With aqueous solutions of trimethylcarbinol, the index of refraction does not exhibit a maximum, and the values are in good agreement with those calculated by means of Gladstone's formula corrected according to Pulfrich. The indices of refraction are greater than the values calculated from the compositions of the solutions. T. H. P.

Synthesis of Methylethylnonylcarbinol. MICHAEL SAYTZEFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 351).—[With UNANOFF.]—*Methylethylnonylcarbinol*, $C_{13}H_{28}O$, prepared by the action of magnesium and ethyl bromide on methyl nonyl ketone in ethereal solution, is a faintly yellow liquid, b. p. 135—137°/15 mm. T. H. P.

Principal Properties of Oxonium Dibromides of Simple Ethers. WLADIMIR W. TSCHELINZEFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 219—225).—The author criticises McIntosh's views (Trans., 1905, **87**, 784; Abstr., 1910, i, 808) on the constitution of the compounds formed by bromine with ethyl and other ethers (compare Tschelinzeff and Konowaloff, Abstr., 1909, i, 353). T. H. P.

Synthesis of Secondary α-Keto-alcohols. D. GAUTHIER (*Compt. rend.*, 1911, **152**, 1100—1102).—α-Keto-alcohols cannot be obtained by the hydrolysis of the corresponding alkyloxy-ketones (Abstr., 1909, i, 353), but are readily prepared by the action of an organo-magnesium halide (2 mols.) on a cyanohydrin (1 mol.).

Pentan-γ-one-β-ol, OH·CHMe·COEt, formed by the action of ethyl magnesium bromide on acetaldehyde cyanohydrin, has b. p. 63°/20 mm.; it reduces Fehling's solution, and gives a *semicarbazone*, m. p. 201°, and a *cyanohydrin*, b. p. about 130°/20 mm. On treatment with magnesium ethyl bromide (2 mols.) it forms *γ-ethylpentane-βγ-diol*, $OH·CHMe·CEt_2·OH$, b. p. 105°/17 mm.

β-Methylhexan-δ-one-γ-ol, $OH·CHPr^{\beta}·COEt$, b. p. 85°/45 mm., forms a *semicarbazone*, m. p. 90°. W. O. W.

Preparation of Diacetone Alcohol from Acetone. ALFRED HOFFMAN (D.R.-P. 229678).—Diacetone alcohol (b. p. 150°) can be readily prepared by passing acetone through powder or nodules of a catalyst, such as calcium hydroxide; the unchanged acetone is subsequently separated from the product by distillation.

F. M. G. M.

Mixed Organo-metallic Derivatives of Zinc and their Use in Organic Syntheses. EDMOND E. BLAISE (*Bull. Soc. chim.*, 1911, [iv], **9**, i—xxvi).—A lecture delivered before the Chemical Society of France on the 18th March, 1911. T. A. H

Catalytic Esterification of Alcohols by Fatty Acids: Case of Formic Acid. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1911, **152**, 1044—1047. Compare this vol., i, 258).—The esterification of formic acid previously stated to be unrealisable by the catalytic method can be effected by employing as catalyst titanium oxide at 150°, or thorium oxide at 200—220°. In the former case, 65% of the acid is esterified when mixed with the vapour of alcohol in equimolecular proportions, but the proportion diminishes as the molecular weight of the alcohol increases. At higher temperatures, the acid decomposes. Methyl, ethyl, propyl, butyl, *iso*butyl, *iso*amyl, and benzyl formates have been prepared by this process, using excess of the alcohol.

Esters may be obtained from secondary and tertiary alcohols by working at temperatures below that at which the hydrocarbon is formed. Equimolecular proportions of *iso*butyric acid and *iso*propyl alcohol with titanium oxide gave 16·5% of the ester at 235° and 37% at 292°; *tert.*-butyl alcohol gave 6% of ester at 235°. W. O. W.

Action of Alkyl Halides on Anhydrides of Monobasic Acids in Presence of Magnesium and Zinc. IVAN VANIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 352—353).—The action of *iso*butyl iodide and magnesium (or zinc) on acetic anhydride yields, not a tertiary alcohol (compare Saytzeff, Abstr., 1907, i, 815), but the secondary methyl*iso*butylcarbinol.

Among the products obtained by the action of *iso*amyl iodide on acetic anhydride in presence of magnesium is a *hydrocarbon*, $C_{12}H_{24}$, b. p. 189—194°. T. H. P.

Direct Synthesis of the Glycerides. II. ITALO BELLUCCI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 235—238. Compare Bellucci and Manzetti, this vol., i, 259; also Gianoli, *ibid.*, i, 349).—Continuing his experiments the author finds that it is unnecessary to employ a vacuum, as previously recommended. When a mixture of the theoretical quantities of oleic acid and glycerol is heated for three hours at 200—250° in a current of carbon dioxide (which does not pass through the liquid), an almost quantitative yield of triolein is obtained. The reaction is much hastened by vigorous stirring. It takes place also in the presence of air, but some discoloration occurs, which necessitates purification of the product. Similar results were obtained with palmitic and stearic acids. R. V. S.

Elaidin and Elaidic Acid. A. GAWALOWSKI (*Chem. Zentr.*, 1911, i, 383; from *Pharm. Post.*, 1910, **43**, 1033).—By decomposing purified lead plaster with hydrochloric acid, the author has obtained stearoelaidic acid, $C_{18}H_{30}O_2$, colourless, pearly crystals, m. p. 38·4°, D^{15} 0·942, and oleoelaidic acid, $C_{18}H_{25}O_2$ (?), in a pure condition. The latter acid is oily, and has m. p. 20·2°, D 0·955. F. B.

Lauronolic and *allo*Campholytic Acids. JULIUS BREDT (*J. pr. Chem.*, 1911, [ii], **83**, 395—400).—[With PAUL MARRES.]—Hitherto two important criteria for the identification of lauronolic acid have been

the facts that its calcium salt forms characteristic crystals and contains $3H_2O$. The authors now show that only $2H_2O$ are present in the calcium salt of lauronolic acid obtained by the dry distillation of camphanic acid, or by the decomposition of chlorocamphoric anhydride by sodium carbonate.

Walker and Henderson's *allo*campholytic acid (Trans., 1895, **67**, 340) forms a calcium salt containing $2H_2O$, and exhibiting the characteristic crystalline form of calcium lauronolate. Formerly *allo*campholytic acid was regarded as identical with γ-lauronolic acid, until Noyes and Taveau showed that the latter is a mixture (Abstr., 1906, i, 397). The preceding analytical result indicates that lauronolic and *allo*campholytic acids are identical, the more so that Walker and Henderson have shown that they yield identical campholactones and bromocampholactones; against this view, however, should be mentioned the different rotations of the two acids, and the different m. p.'s of their amides. Perkin regards *allo*campholytic acid as stereoisomeric with lauronolic acid (Trans., 1898, **73**, 815), whilst Noyes has recently stated that it is a mixture (Abstr., 1910, i, 754).

C. S.

Constitutions of Woringer's Lauronolic Acid, Dihydrolaurolactone (Campholactone), and Laurolene. JULIUS BREDT (*J. pr. Chem.*, 1911, [ii], **83**, 400—405).—A theoretical discussion. Lapworth and Lenton have suggested that during the decomposition of camphanic acid into carbon dioxide, dihydrolaurolactone (campholactone), and lauronolic acid, one of the *gem*-methyl groups wanders to the neighbouring non-methylated carbon atom (Trans., 1900, **77**, 1057; 1901, **79**, 1289). The acceptance of this theory, and of the constitutions of lauronolic acid and dihydrolaurolactone arising therefrom, renders explicable (i) the formation of laurenone from lauronolic acid (Tiemann and Tigges, Abstr., 1901, i, 5), and the conversion of its hydroxylamino-oxime into a nitroso-compound conforming with Piloty's rule; (ii) the production of nitrocampholactone (nitrodihydrolaurolactone) from campholactone by direct nitration (Schryver, Trans., 1898, **73**, 559), and its reduction to a hydroxylaminocampholactone, which can be oxidised to a nitrosocampholactone also conforming to Piloty's rule; (iii) the formation of a nitro*iso*campholactone (nitrodihydro*iso*laurolactone) by the nitration of *iso*campholactone (Noyes and Homberger, this vol., i, 110). Nitrocampholactone and nitro*iso*campholactone are probably stereoisomeric, the isomerism being caused by an interchange in the positions of the nitro- and the methyl groups attached to the same carbon atom.

Lapworth and Lenton's theory gains in probability from the fact that campholactone and *iso*campholactone do not yield a trace of camphoronic acid by oxidation (and therefore no longer retain the *gem*-dimethylated *cyclo*pentane ring of camphoric acid), whereas the lactone, m. p. 161°, obtained by the electrolytic reduction of camphononic acid, behaves quite differently from the two campholactones and is readily converted into camphoronic acid by warming with dilute nitric acid (Bredt, Abstr., 1909, i, 498).

The constitution ascribed to laurolene (obtained as a by-product in

the formation of lauronolic acid) by Eykmann (Abstr., 1907, i, 378), and confirmed by Noyes and Derick (Abstr., 1910, i, 753), is also in harmony with Lapworth and Lenton's theory. C. S.

The Walden Inversion and Substitution Processes. Emil Fischer (*Annalen*, 1911, 381, 123—141).—The author gives a brief résumé of the more important examples of the Walden inversion (compare Walden, Abstr., 1896, i, 139, 205; 1898, i, 127, 178; 1899, ii, 538; E. Fischer, *ibid.*, 1907, i, 192, 381; 1908, i, 324, 387; 1909, i, 359; 1910, i, 622; McKenzie and Wren, Trans., 1910, 97, 1356; McKenzie and Clough, *ibid.*, 1909, 95, 777; 1910, 97, 2564; McKenzie and Humphreys, *ibid.*, 1910, 97, 121).

Most of the examples are met with in the case of α-substituted aliphatic acids and their derivatives. The inversion is not met with in the reactions with *l*-β-hydroxybutyric acid, but is apparently met with in the reaction of nitrous acid on β-aminobutyric acid.

On the whole, the author agrees with the views put forward by Werner (this vol., i, 424). In processes of substitution, it is not necessary that the new group should occupy the same position as the old; it is just as likely that it will take up another position. Whether the configuration of the compound undergoes change during the reaction depends on the nature of the reaction, and, secondly, on the nature of the groups already attached to the asymmetric carbon atom.

Such changes are difficult to represent by means of the usual stereochemical models, and a somewhat modified form of model is recommended, in which the spheres representing the atoms are attached to one another by surfaces covered with stiff bristle.

The author agrees with Michael's view that many, if not all, cases of substitution are preceded by the formation of Kekulé complex molecules. If during the decomposition of such a complex the new substituent enters into a position different from that occupied by the original group, Walden's inversion has taken place. It is extremely difficult in any particular case to say whether inversion has taken place or not. If the inversion is not complete, the result is partial racemisation.

The phenomena met with in the addition of halogens and halogen hydracids to stereoisomeric unsaturated compounds are probably of a similar type, and hence the difficulties met with in attempting to deduce the configurations of unsaturated compounds by means of such reactions. Even in certain cases of the addition of hydroxyl groups to unsaturated compounds, molecular rearrangement may occur; this occurs in the terpene series, although the addition of hydroxyl groups by oxidation to fumaric and malic acids proceeds normally.

In the case of substitution in compounds with several asymmetric carbon atoms, if the product is homogeneous the conclusion can be drawn that the substitution is normal, or complete inversion has occurred. If, on the other hand, a mixture of products is obtained which are not optical antipodes, this indicates partial or complete racemisation of the asymmetric carbon atom affected. Examples from the sugar and terpene series are mentioned. J. J. S.

Action of Zinc on a Mixture of the Haloid Ester and Anhydride of Saturated Monobasic Acids. MICHAEL SAYTZEFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 350—351).—The action of zinc on a mixture of ethyl α-bromo*iso*butyrate and acetic anhydride in ethereal solution yields *β-hydroxy-ααβγγ-pentamethylglutaric acid*, $CO_2H\cdot CMe_2\cdot CMe(OH)\cdot CMe_2\cdot CO_2H$, m. p. 152—161°, the *silver* salt of which was analysed. T. H. P.

Dissociation Constants of Oxalic Acid. JOHANNES E. ENKLAAR (*Chem. Weekblad*, 1911, 8, 375—382. Compare Jellinek, this vol., ii, 362).—For solutions of oxalic acid and sodium hydroxide of various concentrations at 18°, the dissociation constant ($100K$) is 3·4—3·6. From these results the author draws the conclusion that at the concentrations and temperature of the experiments, oxalic acid has the character of a binary electrolyte, and shows no tendency to form complex or acid salts. A. J. W.

Preparation of Normal Oxalic Acid Esters of Lower Aliphatic Alcohols. RUDOLF SCHEUBLE (D.R.-P. 229679).—Methyl or ethyl oxalates can be readily prepared by heating together anhydrous oxalic acid (120 parts) and ethyl alcohol (200 parts) during six hours at 120°, and subsequently removing the excess of alcohol by distillation under diminished pressure; 160 parts of pure ester were thus obtained. F. M. G. M.

Preparation of Oxalates from Alkali Formates. C. F. BOEHRINGER & SÖHNE (D.R.-P. 229853).—Pure colourless sodium oxalate (in 88% yield) can be obtained by heating sodium formate (300 parts) with boric acid or borax (3 parts) in a vessel fitted with an agitator during thirty to forty minutes at a temperature of 360—410°. F. M. G. M.

Reactions of Metallic Oxalates with Some Salts. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. Roy. Belg.*, 1911, 332—334).—Chlorides in general when heated with calcium oxalate give rise to a reaction of the type: $CaC_2O_4 + MCl_2 = CaCl_2 + MO + CO + CO_2$, but if 2 mols. of cupric chloride are used, the following reaction occurs: $CaC_2O_4 + 2CuCl_2 = CaCl_2 + Cu_2Cl_2 + 2CO_2$. With bromides two kinds of reaction may occur: (1) $CaC_2O_4 + MBr_2 = CaBr_2 + MO + CO + CO_2$; (2) $CaC_2O_4 + MBr_2 + O = CaBr_2 + MO + 2CO_2$. Both occur with mercurous bromide, depending on which salt is in excess. The second takes place with lead, cupric, and nickel bromides, and the first with tin and cuprous bromides. With iodides the first type of reaction, referred to under bromides, takes place, whilst with nitrates carbon dioxide only is evolved. The residue from the action of uranyl nitrate contains uranium dioxide, due to the reduction of the trioxide by the carbon formed by decomposition of the oxalate. Sodium hydrogen sulphate heated with calcium oxalate produces carbon monoxide and dioxide. Potassium and sodium sulphates decompose the oxalate only at a high temperature and with difficulty.

T. A. H.

Condensation of Ethyl $\beta\beta$-Dimethylglycidate with Ethyl Bromoacetate. GEORGES DARZENS and J. SEJOURNÉ (*Compt. rend.*, 1911, 152, 1105—1107. Compare this vol., i, 259).—A mixture of ethyl $\beta\beta$-dimethylglycidate and ethyl bromoacetate in benzene solution, on the addition of zinc, yields an organo-zinc compound, which treated in the usual way forms *ethyl* α-*hydroxy*-α-iso*propylsuccinate*, $CO_2Et\cdot CPr^{\beta}(OH)\cdot CH_2\cdot CO_2Et$, b. p. 120—121°/3 mm., 254° under ordinary pressure; the corresponding *acid* has m. p. 139°. The molecular transposition involved in the formation of this ester is accounted for by the preliminary change of the glycidic ester into ethyl dimethylpyruvate, which then condenses normally with the alkyl compound (compare Haller, Abstr., 1906, i, 625). W. O. W.

Preparation of Mesoxalic Esters. ANDRÉ MEYER (*Bull. Soc. chim.*, 1911, [iv], 9, 423—425).—In applying the process of Bouveault and Wahl (Abstr., 1904, i, 556) as modified by Schmitt (Abstr., 1905, i, 508), and subsequently by Curtiss (Abstr., 1906, i, 480; 1908, i, 760), the author finds that the yield of ethyl mesoxalate obtained from ethyl malonate varies within wide limits. The explanation of this is that in the action of nitrogen trioxide on ethyl malonate an oximino-compound is first formed, which by the further action of the trioxide is converted into an unstable substance (compare Curtiss and Tarnowski, Abstr., 1908, i, 760; Lemaire, Abstr., 1909, i, 199), the decomposition of which gives rise to the mesoxalate. In cases where a small yield of the diketonic ester is obtained, the unstable compound remains in the residues from the reaction, and such residues on the application of heat decompose violently, giving a further yield of ethyl mesoxalate.

To obtain good yields the nitrogen trioxide must be dry, and to prevent the deleterious action of moisture a little acetic anhydride may be added to the ethyl malonate. T. A. H.

Destruction of Tartrates by Fermentation. CHARLES ORDONNEAU (*Bull. Soc. chim.*, 1911, [iv], 9, 398—402).—Crude tartrates undergo bacterial anaerobic fermentation with production of salts of acetic acid and of smaller quantities of formic, butyric, and higher acids, but not of propionic acid. Aerobic fermentation also occurs with ultimate formation of carbonates, and not of salts of volatile acids. W. O. W.

Condensations with Ultra-violet Light. RICHARD PRIBRAM and ADOLF FRANKE (*Ber.*, 1911, 44, 1035—1039).—Purified formaldehyde in aqueous solution when exposed to ultra-violet light in a quartz vessel undergoes condensation, forming a product which is partly volatile in steam and reduces Fehling's solution in the cold. A colourless residue remains in the vessel after distillation, which dissolves in water and behaves as glycollaldehyde. No such change takes place in formaldehyde which is not exposed to ultra-violet light.
E. F. A.

Formation of Acetaldehyde by the Pyrogenic Decomposition of Some Oxalates. DOMENICO GANASSINI and EVERARDO SCANDOLA (*Chem. Zentr.*, 1911, i, 63; from *Boll. Soc. Med.-Chirurg., Pavia*, 1910).—Some oxalates, particularly those of barium, strontium, calcium, magnesium, and tin, and the normal oxalates of the alkali metals, yield, when heated in the moist condition, small quantities of acetaldehyde. Oxalic acid itself does not give aldehyde.

The formation of acetaldehyde by heating calcium oxalate may be used for the detection of oxalic acid. The moist precipitate, obtained by the addition of calcium chloride in the presence of acetic acid, is heated in a tube, and the aldehyde detected in the issuing vapours by means of the blue coloration which it gives with paper, moistened with sodium nitroprusside and piperazine. F. B.

Acetaldehyde-hydrazine. ROBERT STOLLÉ (*Ber.*, 1911, 44, 1134—1135).—*Acetaldehyde-hydrazine*, $C_8H_{18}N_6,6H_2O$, the hydrazine analogue of aldehyde-ammonia, is prepared by the interaction of hydrazine hydrate and acetaldehyde in alcoholic solution. It forms small, colourless crystals, m. p. 60°, which lose water when kept for a long time in a vacuum. It is stable towards alkalis, but is decomposed into its constituents when warmed with dilute acids. Its aqueous solutions on being acidified and shaken with benzaldehyde, yield benzalazine. With silver nitrate, it forms an *additive* compound, $C_6H_{18}N_6,3AgNO_3$, and is converted by amyl nitrite and sodium ethoxide in alcoholic solution into an unstable *sodium* salt, the constitution of which has not yet been determined. F. B.

Chloraloxime. F. CARLO PALAZZO and F. FAZIO (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI, 244—246).—Chloraloxime was found by Meyer (Abstr., 1891, 1181) to yield, on decomposition with alkali hydroxide, the theoretical quantity of hydrogen chloride required by the equation: $CCl_3 \cdot CH:NOH + H_2O = CO_2 + HCN + 3HCl$, but only one-half of the theoretical quantities of carbon dioxide and hydrogen cyanide. It is now found that the white substance formed in this process has the formula $C_2H_3O_2NCl_2$, and reacts with hydroxylamine, chlorine being eliminated. An odour resembling that of a nitrile oxide is also observed in the decomposition of chloraloxime with alkali, and it is probable that the first products of the action are chloroform, hydroxylamine, and formic acid, the chloroform and hydroxylamine then reacting to form hydrogen chloride and formonitrile oxide. C. H. D.

The Action of Ammonia and Sodium Carbonate on Different Varieties of Sugar in Dilute Aqueous Solutions. ADOLF JOLLES (*Biochem. Zeitsch.*, 1911, 32, 97—100).—$N/100$ ammonia solution exerts but little action on dilute solutions (0·2 to 1%) of arabinose, dextrose, lævulose, galactose, and maltose at 37° when allowed to remain for twenty-four hours. This is in marked contrast to the action of $N/100$-sodium hydroxide, which, under the same conditions, causes the polarisation to sink to 0°. $N/10$-ammonia acts even less energetically than $N/100$-sodium hydroxide. The action

of sodium carbonate solutions is also considerably weaker than those of sodium hydroxide. S. B. S.

The Composition of the Hexosephosphoric Acid formed by Yeast-juice. I. ARTHUR HARDEN and WILLIAM J. YOUNG (*Biochem. Zeitsch.*, 1911, 32, 173—176).—In reply to Lebedeff (Abstr., 1910, i, 716) it is pointed out that the equation proposed by the authors for the reaction between phosphate and a hexose in the presence of yeast-juice: $2C_6H_{12}O_6 + 2R_2HPO_4 = 2CO_2 + 2C_2H_6O + C_6H_{10}O_4(PO_4R_2)_2 + 2H_2O$ is founded, apart from the composition of the hexosephosphoric acid (following abstract), on the ratios determined between (1) the phosphate added and the carbon dioxide and alcohol produced as a consequence of this addition in the presence of excess of sugar, (2) the sugar used and the carbon dioxide produced in the presence of excess of phosphate.

During the initial period of the fermentation these ratios were found to be $R_2HPO_4 : CO_2$ and $C_6H_{12}O_6 : CO_2$.

The only equation which is compatible with these ratios and with the production of a phosphoric acid derivative containing 6 carbon atoms is that given above. W. J. Y.

The Composition of the Hexosephosphoric Acid formed by Yeast-juice. II. WILLIAM J. YOUNG (*Biochem. Zeitsch.*, 1911, 32, 177—188).—The hexosephosphoric acid was filtered through a Martin gelatin filter in order to ensure its freedom from any colloidal matter, which, according to Lebedeff (Abstr., 1910, i, 716), vitiated the analysis of the salts previously quoted (Abstr., 1909, i, 863). In spite of this treatment the barium salt still corresponded with the formula previously given, $C_6H_{10}O_4(PO_4H_2)_2$.

When hexosephosphoric acid is heated with phenylhydrazine, one phosphoric acid group is split off and a phenylhydrazine salt of a phosphoric acid derivative of a hexosazone formed, which has the composition ascribed to it by von Lebedeff,

$$C_6H_8N_2,H_2PO_4,C_6H_6(OH)_3(N_2HPh)_2.$$

The hexosephosphoric acids derived from dextrose, lævulose, and mannose all yield the same osazone, m. p. 150—152°, thus affording further evidence that the same hexosephosphoric acid is obtained from all these sugars.

The osazone dissolves in sodium hydroxide solution with liberation of one molecule of phenylhydrazine, and, on adding excess of the reagent, the sodium salt of the osazone, $Na_2PO_4\cdot C_6H_6(OH)_3(N_2HPh)_2$, is obtained in yellow needles. When an aqueous solution of this sodium salt is acidified with acetic acid and phenylhydrazine added, the original phenylhydrazine salt of the osazone is formed, whilst if aniline is added in place of phenylhydrazine the corresponding aniline salt is obtained, $C_6H_5\cdot NH_2,H_2PO_4\cdot C_6H_6(OH)_3(N_2HPh)_2$, yellow needles, m. p. 133—135°.

Hexosephosphoric acid forms with phenylhydrazine in the cold an unstable compound, which is a salt of the hydrazine with the hydrazone of hexosediphosphoric acid,

$$(C_6H_5N_2H_3,H_2PO_4)_2,C_6H_7(OH)_3\cdot N_2HPh,$$

white needles, m. p. 115—117°, whilst a similar crystalline compound is formed with *p*-bromophenylhydrazine, m. p. 127—128°. When these hydrazones are heated with more of the hydrazine, 1 molecule of phosphoric acid is liberated, and the corresponding osazone derivative formed.

Hexosephosphoric acid thus contains an active carbonyl group and two phosphoric acid groups, and one of the latter is probably attached to the carbon atom adjacent to the carbonyl group, since it is split off in the formation of the osazone. W. J. Y.

The Destruction of Dextrose by Light. PAUL MAYER (*Biochem. Zeitsch.*, 1911, **32**, 1—9).—Under the influence of light (quartz lamp) in presence of traces of sodium carbonate, dextrose undergoes a characteristic change, which is different to that which it undergoes in the presence of the carbonate alone without exposure to rays. There are formed traces of volatile acids, aldehydes, and glucosone. A complete destruction of the sugar into carbon monoxide and dioxide, etc., under the conditions of the experiments (relatively low temperature) was not observed. S. B. S.

Action of Normal Barium Hydroxide on Dextrose and Galactose. FRED W. UPSON (*Amer. Chem. J.*, 1911, **45**, 458—479).—It is claimed by Kiliani, that the formation of saccharinic acids from the hexoses cannot be effected by the hydroxide of sodium, potassium, or barium, but only by that of calcium, to which he attributes a specific action. It has been found, however, by Nef and also by the author that all alkali hydroxides give analogous results under similar conditions of concentration, but that the proportions of the various saccharinic acids produced vary greatly with the concentration of the reagent.

An investigation has now been made of the action of *N*-barium hydroxide on *d*-galactose and dextrose. Some of the saccharinic acids were isolated which were obtained by Nef (Abstr., 1910, i, 714) by the action of 8*N*-sodium hydroxide on these sugars, but whereas Nef isolated large quantities of *α*- and *β*-*meta*-saccharinic and *α*- and *β*-*iso*saccharinic acids with six carbon atoms, only small amounts of the first three of these acids were obtained in the present case, whilst relatively larger amounts of *dl*-lactic and *dl*-*αγ*-dihydroxybutyric acids were produced. The quantity of optically inactive C_5 and C_6 saccharinic acids, formed from inactive pentoses and hexoses produced by synthetic condensation, was also relatively larger and rendered the detection and isolation of the active C_6 saccharinic acids exceedingly difficult E. G.

Action of (1) Hydracids, (2) Formic and Acetic Acids, in Increasing Proportions, on Starch and Dextrin. WILLIAM OECHSNER DE CONINCK and A. RAYNAUD (*Bull. Acad. Roy. Belg.*, 1911, 213—215, 335—337. Compare Abstr., 1910, i, 655, and this vol., i, 181).—When equal quantities of starch or dextrin are heated with increasing quantities of hydrochloric or hydrobromic acid for the same length of time, the amount of hydrolysis is proportional to the

concentration of acid employed, but the quantity of dextrin hydrolysed is always greater than that of starch hydrolysed.

With acetic and formic acids as hydrolytic agents, on the contrary, whilst the amount of hydrolysis is still proportional to the concentration of the acid, the quantities of dextrin and starch hydrolysed are practically equal, thus establishing a marked difference between hydrolysis as effected by mineral and organic acids. T. A. H.

Ethylene- and Propylene-diammonium Aurihalides. Alexander Gutbier and C. J. Obermaier (*Chem. Zentr.*, 1911, i, 540—541; from *Sitzungsber.*, *Physik.-med. Soz.*, *Erlangen*, 42).—A description of the preparation and properties of the aurichlorides and auribromides. *Ethylenediammonium aurichloride*, $C_2H_8N_2,2HAuCl_4,2H_2O$, yellow, tabular crystals of monoclinic habit; the *auribromide*,

$$C_2H_8N_2,2HAuBr_4,2H_2O,$$

red to brownish-red lamellæ, possibly monoclinic.

Propylenediammonium aurichloride, $C_3H_{10}N_2,2HAuCl_4,2H_2O$, and *propylenediammonium auribromide*, $C_3H_{10}N_2,2HAuBr_4,H_2O$, resemble the corresponding ethylenediamine compounds. F. B.

Spatial Change of Position During Reactions of Stereoisomeric Compounds. Alfred Werner (*Ber.*, 1911, 44, 873—882).—The author has studied the reactions of a large number of stereoisomeric diethylenediaminecobalt salts of the general formula $[A_2Co\ en_2]X_n$, and finds that the replacement of an acid group in co-ordinative combination with the metallic atom by ammonia, water, etc., is frequently accompanied by a change in the spatial configuration, the new group taking up a different position to that originally occupied by the group which it has replaced.

Thus *trans*-dichloro- and *trans*-dibromo-diethylenediaminecobalt salts are almost quantitatively converted into *cis*-chloro- and *cis*-bromo-amminediethylenediaminecobalt salts by the action of strong aqueous ammonia; *trans*-dichlorodiethylenediaminecobalt chloride when dissolved in water is transformed into *cis*-chloroaquodiethylenediaminecobalt chloride.

A similar change of configuration is also found to occur during substitution reactions. The following examples are given: *trans*-chloro*iso*thiocyanodiethylenediaminecobalt salts, when treated with strong aqueous ammonia, yield *cis*-hydroxylo*iso*thiocyanodiethylenediamine salts, which may be isolated in the form of aquo-salts, $\left[\begin{matrix}SCN\\H_2O\end{matrix}\ Co\ en_2\right]X_2$; *trans*-dibromodiethylenediaminecobalt bromide is quantitatively formed by dissolving *cis*-chlorobromodiethylenediaminecobalt bromide in hydrobromic acid; when *cis*-chloroamminediethylenediaminecobalt nitrite is treated with sodium nitrite, both *cis*- and *trans*-nitroamminediethylenediaminecobalt nitrites are obtained.

Change of configuration also takes place during reactions in which ammonia, water, etc., are expelled from combination with the metallic atom. Thus *trans*-chloronitrodiethylenediaminecobalt nitrite is obtained from *cis*-chloroamminediethylenediaminecobalt nitrite by

heating in concentrated aqueous solution, whilst *trans*-diaquodiethylenediaminecobalt chloride when kept is transformed into *cis*-dichlorodiethylenediaminecobalt chloride.

That this change of configuration is not associated with the transformation of the less stable into the more stable form is proved by the fact that the changes lead as frequently from the cis- to the trans-group as in the reverse direction. This view is further supported by the following reactions: (1) Salts of the *trans*-dichlorodiethylenediamine group yield, with potassium hydroxide, *cis*-hydroxyloaquodiethylenediaminecobalt salts, whilst the stereoisomeric *cis*-dichloro-compounds are converted by ammonia into salts of the *trans*-hydroxyloaquodiethylenediamine group; (2) both *cis*- and *trans-iso*thiocyanoamminediethylenediaminecobalt salts when warmed with potassium thiocyanate give rise exclusively to salts of the *trans*-di*iso*thiocyanodiethylenediaminecobalt group; the stereoisomeric chloro*iso*thiocyanodiethylenediaminecobalt chlorides are converted by liquid ammonia into a mixture of *cis*- and *trans-iso*thiocyanoamminediethylenediaminecobalt chlorides, in approximately the same proportions.

An explanation of these strange transformations was found from a consideration of the difference in the behaviour exhibited by various salts belonging to the same group. When chloroamminediethylenediaminecobalt nitrite and thiocyanate are warmed in concentrated aqueous solution, loss of ammonia takes place, whilst with other salts of the same group no action occurs. Diaquotetramminecobalt sulphate undergoes no change on keeping, whereas the bromide and chloride are completely converted into $\left[{}^{Br}_{H_2O}Co(NH_3)_4\right]Br_2$ and $\left[{}^{Cl}_{H_2O}Co(NH_3)_4\right]Cl_2$ respectively.

Differences in the behaviour of acid groups attached to the metallic atom have also been observed. Whilst salts of the chloro*iso*thiocyanodiethylenediaminecobalt group are quantitatively transformed into *iso*thiocyanoamminediethylenediaminecobalt salts, and salts of the nitratonitrodiethylenediaminecobalt group when subjected to the same treatment yield nitroamminediethylenediamine salts, di*iso*thiocyano- and dinitro-diethylenediaminecobalt salts remain unchanged.

From the changes illustrated in the above examples, the author draws the following conclusions: (1) The central atom of a complex radicle exerts an attraction on groups not directly attached to it, tending to bring them into co-ordinative combination with the central atom. (2) The magnitude of this attraction depends on the nature of the groups. (3) The attraction will be exercised in a definite spatial direction, and this will therefore define the position taken up by the new group. (4) In the case of a co-ordinatively saturated compound, a new group can only enter into union with the central atom by the expulsion of another group, and that group will therefore be expelled which is least firmly attached.

Since the spatial position of the entering group is independent of that originally occupied by the group expelled, an explanation is thus afforded of the changes in the spatial configuration described above. The formation of a mixture of stereoisomerides in many reactions is

explained on the assumption that the attraction exerted by the central atom is exercised in different spatial directions.

In the case of substitution reactions proceeding according to the scheme: $AX + BY = AY + BX$, an additive compound is first produced; the group X becomes, thereby, less firmly attached, and, owing to the attraction exerted on the group Y by the central atom, is finally expelled, the group Y then entering into co-ordinative union with the central atom.

Examples are given in which intermediate additive compounds have been isolated. The stereoisomeric *iso*thiocyanoaquodiethylenediaminecobalt salts, $\left[\begin{smallmatrix}SCN\\H_2O\end{smallmatrix}Co\ en_2\right]X_2$, yield, with silver nitrate, stable crystalline *silver* salts, $\left[\begin{smallmatrix}AgSCN\\H_2O\end{smallmatrix}Co\ en_2\right]X_3$, from which silver thiocyanate is removed only on boiling. *trans*-Chloro*iso*thiocyanodiethylenediaminecobalt nitrate, $\left[\begin{smallmatrix}SCN\\Cl\end{smallmatrix}Co\ en_2\right]NO_3$, forms with silver nitrate an *additive* compound, $\left[\begin{smallmatrix}SCN\\AgCl\end{smallmatrix}Co\ en_2\right](NO_3)_2$, which is soluble in cold water, is precipitated on the addition of nitric acid, and loses silver chloride when heated in aqueous solution.

By treating chloroamminediethylenediaminecobalt nitrite with sodium nitrite, an *intermediate* product, $\left[\begin{smallmatrix}NaCl\\NH_3\end{smallmatrix}Co\ en_2\right](NO_2)_3$, is obtained; in concentrated solution this loses ammonia, forming chloronitrodiethylenediaminecobalt nitrite, whilst in dilute solution sodium chloride is removed with the formation of nitroamminediethylenediaminecobalt nitrite.

The author has extended these ideas on the process of substitution and the change of spatial configuration to the reactions of organic compounds, and, on the assumption of the intermediate formation of additive compounds, gives an explanation of the Walden inversion.

F. B.

New Synthesis of γ-Homocholine. ERNST BERLIN (*Chem. Zentr.*, 1911, i, 475; from *Zentr. Physiol.*, 1910, **24**, 779—780).—γ-Homocholine may be prepared by methylating β-aminopropyl alcohol with methyl iodide; it is isolated by precipitating it with phosphotungstic acid and conversion into the *aurichloride*, $C_6H_{16}ONCl,AuCl_3$, m. p. 163°.

Morley's β-homocholine (Abstr., 1881, 151) is identical with that described by Malengreau and Lebailly (Abstr., 1910, i, 545). F. B.

Homocholine Ether. ERNST BERLIN (*Chem. Zentr.*, 1911, i, 475; from *Zentr. Physiol.*, 1910, **24**, 929—930).—In the preparation of γ-homocholine by the interaction of trimethylamine and trimethylenechlorohydrin, and subsequent isolation by means of the aurichloride, a salt sparingly soluble in water was obtained. On converting this into the platinichloride it was separated into hexamethyltrimethylenediamine platinichloride and *homocholine ether platinichloride*,

$$O(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3Cl)_2,PtCl_4,$$

m. p. 258—260°. The *aurichloride*, $C_{12}H_{30}ON_2Cl_2,2AuCl_3$, has m. p. 230—232°. F. B.

The Action of Mercuric Chloride on Glycine. MAX SIEGFRIED (*Ber. K. Sachs. Ges. Wiss. Math.-phys. Klasse*, 1910, **62**, 57—68).—An account of numerous experiments on the action of mercuric chloride on glycine under greatly varying conditions; the evolved ammonia was estimated and various organic products analysed.

Iminodiacetic acid was obtained and shown to be identical with that previously prepared from chloroacetic acid; it yields a *silver* salt, $C_4H_5O_4NAg_2$, and a blue *copper* salt. The action of mercuric chloride and mercury acetamide on glycine was also studied.

F. M. G. M.

$\alpha\alpha'$-Ethylenedi-iminodi*iso*butyric Acid. N. SCHLESINGER (*Ber.*, 1911, **44**, 1135—1137).—*$\alpha\alpha'$-Ethylenedi-iminodi*iso*butyronitrile hydrochloride*, $C_2H_4(NH{\cdot}CMe_2{\cdot}CN)_2,2HCl$, is precipitated in the form of a white, crystalline powder by passing hydrogen chloride into the ethereal solution of the product obtained by the interaction of potassium cyanide, ethylenediamine hydrochloride, and acetone in the presence of a small quantity of water. It has m. p. 93—96° (sintering at 93°), and is hydrolysed by hydrochloric acid to *$\alpha\alpha'$-ethylenedi-iminoisobutyric acid hydrochloride*, $C_{10}H_{20}O_4N_2,HCl,2H_2O$, which crystallises in lustrous needles, m. p. above 245°.

The *ethyl* ester, $C_{14}H_{28}O_4N_2$, prepared from the preceding compound by Fischer's method, has b. p. 171—172°/15 mm., D_4^{20} 0·9934, n_D^{20} 1·4432, and yields a crystalline *hydrochloride*.

*$\alpha\alpha'$-Ethylenedi-iminodi*iso*butyric acid*, $C_2H_4(NH{\cdot}CMe_2{\cdot}CO_2H)_2$, obtained from the ethyl ester by boiling with water, is a white, crystalline powder, and gives a blue *copper* salt, $C_{10}H_{18}O_4N_2Cu$.

Other ketones and also aldehydes react with potassium cyanide and ethylenediamine hydrochloride in a similar manner. F. B.

Action of *iso*Amyl Nitrite on Amines and Amides. S. SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1—17).—In order to throw light on the reaction taking place between amines (or amides) and nitrous acid or nitrosyl chloride, the author has replaced the latter by *iso*amyl nitrite, which has the advantage of reacting in absence of water or mineral acid.

With acetamide, *iso*amyl nitrite yields *iso*amyl alcohol, acetic acid, water, nitrogen, and *iso*amyl acetate. With carbamide, *iso*amyl alcohol, carbon dioxide, water, nitrogen, and *iso*amyl carbamate. With *iso*amylamine, *iso*amyl alcohol, nitrogen, and a large proportion of secondary products with high b. p. With dibenzylamine, dibenzylnitrosoamine and *iso*amyl alcohol; and with diphenylamine, diphenylnitrosoamine and *iso*amyl alcohol.

Comparison of these results with those obtained with (1) ammonia and esters (or anhydrides or chloroanhydrides) of organic acids; (2) amines and nitrous acid; (3) amines and nitrosyl chloride, and (4) hydrazine and ethyl nitrite, indicates the reactions in the above cases to be expressed by the following equations:

With acetamide:

$$CH_3\cdot CO\cdot NH_2 + C_5H_{11}O\cdot NO = CH_3\cdot CO\cdot NH_2(NO)\cdot O\cdot C_5H_{11} = CH_3\cdot CO\cdot NH\cdot NO + C_5H_{11}\cdot OH = CH_3\cdot CO_2H + N_2 + C_5H_{11}\cdot OH;$$
$$CH_3\cdot CO_2H + C_5H_{11}\cdot OH = CH_3\cdot CO_2\cdot C_5H_{11} + H_2O.$$

With carbamide:

(I) $NH_2\cdot CO\cdot NH_2 + 2C_5H_{11}O\cdot NO = CO[\cdot NH_2(NO)\cdot O\cdot C_5H_{11}]_2 = CO(\cdot NH\cdot NO)_2 + 2C_5H_{11}\cdot OH$; $CO(\cdot NH\cdot NO)_2 = CO(\cdot N{:}N\cdot OH)_2 = CO_2 + H_2O + 2N_2$.

(II) $NH_2\cdot CO\cdot NH_2 + C_5H_{11}O\cdot NO = NH_2\cdot CO\cdot NH_2(NO)\cdot O\cdot C_5H_{11} = NH_2\cdot CO\cdot NH\cdot NO + C_5H_{11}\cdot OH$; $NH_2\cdot CO\cdot NH\cdot NO = NH_2\cdot CO_2H + N_2$, and $NH_2\cdot CO_2H + C_5H_{11}\cdot OH = NH_2\cdot CO_2\cdot C_5H_{11} + H_2O$.

With *iso*amylamine:

$$C_5H_{11}\cdot NH_2 + C_5H_{11}O\cdot NO = C_5H_{11}\cdot NH_2(NO)\cdot O\cdot C_5H_{11} = C_5H_{11}\cdot NH\cdot NO + C_5H_{11}\cdot OH = 2C_5H_{11}\cdot OH + N_2.$$

With dibenzylamine or diphenylamine: $NR_2H + C_5H_{11}O\cdot NO = NO\cdot NR_2H\cdot O\cdot C_5H_{11} = NR_2\cdot NO + C_5H_{11}\cdot OH$, where $R = Ph$ or CH_2Ph.

T. H. P.

The Constitution of the Hydroxamic Acids. F. Carlo Palazzo (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI, 249—252).—The conductivity of the hydroxamic acids shows that all have a similar constitution; it is therefore sufficient to examine one such acid in detail, and formohydroxamic acid has been chosen. The reactions are discussed in order to show that the formula $\begin{matrix}CH_2\\ |\\ O\end{matrix}\!\!>\!N\cdot OH$ best expresses its behaviour.

C. H. D.

Oxalo-monohydroxamic Acid. F. Carlo Palazzo and E. Oliveri-Mandala (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI, 247—248).—Compounds of the type $CHX{:}NOH$, where $X = Cl$, Br, I, NO_2 or SCN, decompose at about 0°. *Oxalo-monohydroxamic acid*, $CO_2H\cdot C(OH){:}NOH$, obtained by Dimroth and Dienstbach (Abstr., 1909, i, 63) only in the form of a salt, may be prepared by mixing concentrated aqueous solutions of hydroxylamine and sodium methyl oxalate. The pure sodium salt crystallises on cooling. After conversion into the copper salt and decomposition by hydrogen sulphide, the acid is obtained, m. p. 118°. The *silver* salt,

$$C_2HO_4NAg_2,$$

like the corresponding mercury salt, is not convertible into a fulminate, and the authors regard this as a further proof that hydroxamic acids have the constitution $R\cdot \underset{\diagdown O \diagup}{CH\cdot N}\cdot OH$ (compare preceding abstract).

C. H. D

Some Hydroxamic Acids of the Pyrone Series. E. Oliveri-Mandala (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI, 303—304).—In view of the behaviour of pyrone derivatives with hydroxylamine (Azzarello, Abstr., 1905, i, 916) the action of hydroxylamine on the esters of chelidonic and triethylmeconic acids has been examined. It is found that both compounds yield hydroxamic acids, whilst ethyl diethylmeconate remains unchanged.

C. H. D.

Some New Data on the Preparation of Biguanide. ADRIANO OSTROGOVICH (*Chem. Zentr.*, 1910, ii, 1890; from *Bul. Soc. Ştiinţe, Bucureşti*, 1910, 19, 641—647).—The replacement of ammonium chloride by ammonium iodide in the preparation of biguanide from dicyanodiamide (compare Bamberger and Dieckmann, Abstr., 1892, 737) raises the yield from 21—23% to 45%. The yield is also increased by using ammonium chloride, but not to the same extent as when the iodide is employed. F. B.

Action of Hydrogen Sulphide on Fulminic Acid. LIVIO CAMBI (*Gazzetta*, 1911, 41, i, 166—173).—Nef (Abstr., 1895, i, 9) found that the action of hydrogen sulphide, in the cold, on silver fulminate suspended in water results in the formation of an unstable compound, which decomposes, giving silver sulphide, which he supposed to be the silver salt of thioformhydroxamic acid, $SH\cdot CH\colon NOAg$. Ammonium thiocyanate forms the principal product of the action of hydrogen sulphide, in presence of water, on fulminates of the heavy metals, and the formation of this salt may be readily explained as due to the decomposition of the initial product, thioformhydroxamic acid, in the two following ways: (1) $SH\cdot CH\colon NOH = SH\cdot CN + H_2O$ and (2) $SH\cdot CH\colon NOH \longrightarrow SH\cdot CO\cdot NH_2 \longrightarrow COS + NH_3$.

The author has confirmed the formation of thioformhydroxamic acid in the action of hydrogen sulphide on mercury fulminate, as the solution, after removal of the mercuric sulphide, gives an intense, violet-blue coloration with ferric chloride (compare Abstr., 1909, i, 646). The acid may also be obtained by treating the product of the interaction of chloroform (1 mol.) and sodium sulphide (2 mols.) with hydroxylamine.

Benzyl thioformhydroxamate, $CH_2Ph\cdot S\cdot CH\colon NOH$, crystallises in nacreous scales or elongated prisms, m. p. 144—146°, has the normal molecular weight in boiling alcohol, and, when heated in aqueous alcoholic solution with hydrochloric acid, decomposes according to the equation:

$$C_7H_7\cdot S\cdot CH\colon NOH + 2H_2O = H\cdot CO_2H + NH_2\cdot OH + SH\cdot CH_2Ph.$$

The *sodium, cadmium, lead, mercuric, nickel, cobalt, cupric,* and *silver* salts of the acid have been prepared. In solution the acid decomposes more or less rapidly into thiocyanic acid and water, whilst the sodium salt gives ammonia and carbon oxysulphide. The benzyl ether melts without decomposition, but when fused at 80—85° with benzoic anhydride, it decomposes with formation of benzyl thiocyanate.

T. H. P.

The Existence of Other Gaseous Compounds of Carbon and Nitrogen Besides Cyanogen. ALEXANDER P. LIDOFF (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IVAI, 315).—When cyanogen is heated in contact with iron, the gas increases in volume, and a part becomes soluble in acid cuprous chloride. When nitrogen is passed over heated charcoal, an increase of volume also takes place, and a part of the gas becomes soluble in acid cuprous chloride. The soluble gas is oxidised by one-half its volume of oxygen, but the product is lighter than carbon dioxide. C. H. D.

An Isomeride of Potassium Ferricyanide. ITALO BELLUCCI and G. SABATINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 176—181).—By the application of Freund's reaction (Abstr., 1888, 571) by means of which both the ferrocyanide and the ferricyanide of potassium yield the ferroimino-ether, $H_4FeC_6{<}{}^{(NH)_6}_{(OEt)_6}$,2HCl, the authors propose to elucidate the constitution of the green, isomeric potassium ferricyanide obtained by Locke and Edwards (Abstr., 1899, i, 557). R. V. S.

Case of Structural Isomerism in the Metallic Cyanides. ITALO BELLUCCI and G. SABATINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 239—243. Compare preceding abstract).—The amounts of iodine liberated by α- and β-potassium ferricyanides agree with what is required by the constitutions previously suggested. In very dilute solutions both salts are completely dissociated into four ions. The α-ferricyanide yields the ferroimino-ether, $C_{18}H_{41}O_6N_6FeCl_2$, so that all its cyanogen groups take part in Pinner's reaction. The β-ferricyanide does not enter into this reaction. The α-ferricyanide evolves hydrogen cyanide when boiled with potassium persulphate, whilst the β-form yields cyanic acid in those circumstances. These facts support the view previously advanced that the α-ferricyanide has the nitrilic, and the β-form the *iso*nitrilic, constitution. When an aqueous solution of the β-ferricyanide is treated with potassium hydroxide or with ammonia, its colour changes from green into the yellow characteristic of the α-form. R. V. S.

So-called Perferricyanides. LIVIO CAMBI (*Gazzetta*, 1911, 41, i, 157—166).—When a ferrocyanide is converted into ferricyanide by the action of chlorine, prolonged action of the halogen results in attack of the ferricyanide with formation of an intensely violet solution. Uncertainty exists, however, as to the nature of the compound formed. According to Borg (this Journ., 1876, i, 907) a perferricyanide or "black prussiate" is obtained having the formula $K_2Fe(CN)_6$, which was regarded as probably correct by Skraup (Abstr., 1877, 32, 597), and is quoted by Dammer (*Handbuch der anorg. Chemie*, 3, 378) and by Moissan (*Traité de Chimie Min.*, 4, 417). But Beilstein's *Handbuch* (3rd edition, 1, 1425; *Ergänzungsbände*, 1, 797) gives the formula $K_2Fe(CN)_5,H_2O$, which is agreement with Skraup's values for the relation Fe : C. The nature of the perferricyanide is rendered still more uncertain by the existence of sodium aquopentacyanoferrate (compare Hofmann, Abstr., 1900, i, 591).

The author has prepared potassium perferricyanide by Skraup's method, the salt being purified by repeated precipitation from aqueous solution by means of alcohol. This procedure yields a violet, amorphous powder, for which the relation Fe : K = 1 : 2; it liberates, from potassium iodide, one atom of iodine per atom of iron, whereas a compound having the formula given by Borg (*vide supra*) should liberate two atoms of iodine: $H_2Fe^{IV}(CN)_6 + 2HI = H_4Fe^{II}(CN)_6 + I_2$.

The reactions of potassium perferricyanide correspond with those of the pentacyanoferrates, and in solution the salt has a colour equal to

that of $Na_2[Fe(CN)_5,H_2O]$, prepared by Hofmann's method. The formation of the perferricyanide is hence expressed by the equation: $K_3Fe'''(CN)_6 + Cl_2 = K_2Fe'''(CN)_5 + KCl + CN{\cdot}Cl$. The same reaction takes place if the chlorine is replaced by sodium chlorate and hydrochloric acid.

When reduced by means of alkaline hydroxylamine hydrochloride solution, alkali sulphide or formaldehyde and acetone in presence of alkali, potassium perferricyanide yields *potassium aquopentacyanoferrite*, $K_3[Fe(CN)_5,H_2O]$, the properties of which are similar to those of the corresponding sodium salt (compare Hofmann, *loc. cit.*). Reduction by means of excess of potassium sulphite in presence of potassium hydroxide yields *potassium ferrososulphitocyanide*, $K_5[Fe(CN)_5SO_3]$, which crystallises from aqueous alcohol in small, yellow prisms, and exhibits all the reactions of the pentacyanoferrites.

The formation of the "black prussiate" is regarded as occurring in the two stages: (1) $[Fe(CN)_6]''' + Cl_2 = [Fe(CN)_5Cl]''' + CN{\cdot}Cl$; (2) $[Fe^{III}(CN)_5Cl]''' + H_2O = [Fe^{II}(CN)_5,H_2O]'' + Cl'$. T. H. P.

Crystallographic-optical Investigations [Double Platinocyanides and Picrates]. HEINRICH BAUMHAUER (*Zeitsch. Kryst. Min.*, 1911, 49, 113—132. Compare Abstr., 1907, ii, 689, 907; 1909, ii, 841).—Sodium platinocyanide, $Na_2Pt(CN)_4,3H_2O$, triclinic

$$[a:b:c = 0.5879:1:0.4757;\ \alpha = 87^\circ 42',\ \beta = 94^\circ 56\tfrac{3}{4}',\ \gamma = 90^\circ 59\tfrac{1}{2}'].$$

Rubidium platinocyanide, $Rb_2Pt(CN)_4,3H_2O(?)$, monoclinic

$$[a:b:c = 0.9313:1:0.5325;\ \beta = 99^\circ 48\tfrac{1}{4}'].$$

Optical determinations are given for these and also for the strontium and yttrium salts. The following, and other, details are collected respecting the double platinocyanides:

	Crystal system.	Colour.	Fluorescence.	Metallic sheen.
Sodium salt	Triclinic	Colourless	None	None
Strontium salt	Monoclinic	Colourless	Violet	None
Rubidium ,,	Monoclinic	Pale green	Sky-blue	None
Calcium ,,	Rhombic	Greenish-yellow	Green	Violet to blue
Barium ,,	Monoclinic	Yellow	Green	
Rubidium-lithium salt	Rhombic	Yellow	Green	Blue
Potassium-sodium salt	Monoclinic	Orange	Green	Purple-red to blue
Potassium-lithium ,,	Rhombic	Orange-red	Yellow	Blue
Yttrium ,,	Rhombic	Dark red	Cherry-red	Green

Potassium picrate, $C_6H_2(NO_2)_3{\cdot}OK$, rhombic

$$[a:b:c = 0.6972:1:0.3723];$$

ammonium picrate, $C_6H_2(NO_2)_3{\cdot}ONH_4$, rhombic

$$[a:b:c = 0.6799:1:0.3600].$$

L. J. S.

Constitution of Benzene from the Point of View of the Corpuscular-atomic Conception of Positive and Negative Valency. I. An Interpretation of the Crum Brown-Gibson Rule. II. Dynamical Formulæ and the Ultra-violet Absorption Spectrum of Benzene. III. Dynamical Formulæ and the Ultra-violet Absorption Spectrum of Naphthalene. HARRY S. FRY (*Zeitsch. physikal. Chem.*, 1911, 76, 385—397, 398—412, 591—600).—I. The author uses the conception of the atomic nature

of electricity, as developed by J. J. Thomson, Nernst, and Ramsay, and assumes that the atoms in a molecule are held together by the attraction of contrary electric charges. In the hydrogen molecule, for instance, one of the atoms has a positive, the other a negative, charge, and hence hydrogen can function as a univalent positive or negative element. On the same basis, the carbon atom having four valencies which may be all positive, all negative, or partly positive partly negative, gives five different types. The possible modes of representing benzene on this basis are then considered, and it is shown (1) that there is a structural basis for the similarity in behaviour of the ortho- and para-positions in contrast to the meta-position; (2) the electronic formula, like Collie's benzene formula, leads to the conclusion that there are two groups of hydrogen atoms; it is suggested that the 1:3:5 atoms are negative, the 2:4:6 atoms positive; (3) an explanation of the Crum Brown-Gibson rule can be given. The latter explanation depends upon the assumption of a difference between X in the compounds HX and HOX; in the former it is negative, in the latter positive. In a mono-substituted benzene derivative, C_6H_5X, therefore, X may be positive or negative, according as it is a derivative of HOX or HX. For details as to the application of these conceptions, the original paper should be consulted.

II. The views developed in the previous paper are applied to the interpretation of the absorption spectrum of benzene. Using Collie's space formula for benzene, it is shown that there are seven separate systems in dynamical equilibrium, and that there is a numerical relationship between these electronic isomerides and the vibration frequency of each of the seven bands in the ultra-violet region of the benzene spectrum. This results lends support to the suggestion of Baly and Desch (Trans., 1905, 87, 766) that the bands are connected in some way with the vibrations of the benzene molecule.

III. The above conceptions are applied to the interpretation of the ultra-violet absorption spectrum of naphthalene, and in this case also it has been shown that there is a quantitative relationship between the vibration frequencies of the absorption bands and the number of transitions which can take place between the different electronic isomerides. G. S.

Preparation of Organic Iodo-compounds from the Corresponding Chloro- and Bromo-derivatives by the Action of Alkali Iodides. KNOLL & Co. (D.R.-P. 230172).—The replacement of chlorine or bromine by iodine in organic compounds by treatment with an acetone solution of an alkali iodide has previously been described (compare Finkelstein, Abstr., 1910, i, 453); this reaction has now been extended to the preparation of iodoacetic, iodopropionic, and iodo*iso*valeric acids from the corresponding bromo-compounds. $\omega\omega'$-Dibromo-*o*-xylene yielded *$\omega\omega'$-di-iodo-*o*-xylene*, m. p. 110°; whilst *$\omega\omega'$-di-iodo-*m- and *$\omega\omega'$-di-iodo-*p-*xylene*, m. p. 106° and 174° respectively, *tetraiodo-*m-*xylene*, m. p. 140°, p-*nitrobenzyl iodide*, m. p. 124°, and *ω-iodo-*p-*toluic acid*, m. p. 335°, were also prepared. F. M. G. M.

Action of Ethyl Alcohol on Arylsulphonyl Chlorides. R. GOUBAU (*Bull. Acad. Roy. Belg.*, 1911, 233—252).—The action of alcohol on benzenesulphonyl, *o*-, *m*-, and *p*-toluenesulphonyl, and *p*-chloro-, *p*-bromo- and *p*-iodo-benzenesulphonyl chlorides has been studied with a view to the determination of the nature of the reaction in each case, and the experimental results are tabulated in the original. With cold dilute solutions of the sulphonyl chlorides, hydrochloric acid and the ethyl ester of the sulphonic acid are formed, but on warming, the ester is saponified by the excess of alcohol, ethyl ether and the sulphonic acid being produced. At 30° and for very dilute solutions in dry alcohol the second reaction is negligible. The first reaction is unimolecular, and Wilhelmy's formula is applicable; the value of k increases especially towards the end of the reaction. This is due to autocatalysis induced by the hydrochloric acid formed, since if this acid is added at the beginning of the experiment the reaction is greatly accelerated. The chief conclusions drawn from the results are that (1) for sufficiently dilute solutions the first reaction may be regarded as unimolecular, (2) the value of the ratio k_{t+10}/k_t is 2·63; (3) the group $-CH_3$, replacing a nuclear hydrogen atom, diminishes the velocity of reaction to the greatest extent in the meta-position, less in the para-position, and scarcely at all in the ortho-position with respect to the chlorine atom; (4) the replacement of a nuclear hydrogen atom by a halogen causes acceleration of the reaction, the effect increasing with the atomic weight of the substituent. T. A. H.

Supposed Action of Organo-magnesium Compounds on the Vinyl Group of the Cinchona Alkaloids and of Styrene. BERNARDO ODDO (*Gazzetta*, 1911, **41**, i, 320—329).—The author criticises Comanducci's work on the action of organo-magnesium compounds on styrene and cinchotoxine (Abstr., 1909, i, 409; *Gazzetta*, 1910, **40**, i, 582, 584). His experiments with styrene and with cinchonine show that in neither case does the vinyl group react with organo-magnesium compounds. T. H. P.

***o*:*o*′-Dinitrotolane.** ALFRED KLIEGL and KARL HAAS (*Ber.*, 1911, **44**, 1209—1218).—The reaction between sodium ethoxide and alcoholic *o*-nitrobenzylidene chloride at 35—40° yields o:o′-*dinitrotolane*, $C_{14}H_8O_4N_2$, yellow needles, m. p. 189—189·5°, the identity of which is proved by the formation of the same substance by heating o:o′-*dinitrostilbene dichloride*, m. p. 152—152·5°, with alcoholic sodium ethoxide. By reduction with alcoholic hydrogen chloride and stannous chloride, it yields o:o′-*diaminotolane*, $C_{14}H_{12}N_2$, m. p. 154°, colourless leaflets with a blue fluorescence, which is best purified through the *picrate*. When heated with concentrated sulphuric acid on the water-bath, *o*:*o*′-diaminotolane changes into the isomeric 2-o-*aminophenylindole*, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CH}{NH}}{>}C\cdot C_6H_4\cdot NH_2$, m. p. 154°, the *picrate* of which, m. p. about 187°, is also obtained by heating *o*:*o*′-diaminotolane picrate at 140—143°.

By oxidation with chromic and acetic acids, *o*:*o*′-dinitrotolane yields *o*:*o*′-dinitrobenzil, yellow prisms, m. p. 206°, which is shown to be identical with Golubeff's *iso*dinitrobenzil, obtained by the oxidation of

the product formed by the action of nitric acid, D 1·52, on deoxybenzoin. Popovici's so-called $o:o'$-dinitrobenzil, m. p. 151° (Abstr., 1907, i, 628), cannot be such, since it is colourless.

Sodium methoxide and methyl alcoholic *o*-nitrobenzylidene chloride yield, not a tolane derivative, but *o*-nitrobenzylidenedimethyl acetal in the normal manner. *m*-Nitrobenzylidene chloride reacts with sodium ethoxide in ethyl alcohol in the normal way. C. S.

Preparation of 1 : 5-Dichloronaphthalene-3-sulphonic Acid and of 1 : 4-Dichloronaphthalene-6-sulphonic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 229912).—When the mixture of 1 : 4- and 1 : 5-dichloronaphthalenes obtained by the chlorination of naphthalene is sulphonated, it yields 1 : 4-dichloronaphthalene-6-sulphonic acid and 1 : 5-dichloronaphthalene-3-sulphonic acid, which can be separated by the different solubilities of their sodium salts; sodium 1 : 4-dichloronaphthalene-6-sulphonate is the more insoluble, as are also its magnesium and alkaline earth salts. F. M. G. M.

Triphenylmethyl and Triphenylcarbinol. WILHELM SCHLENK, LEOPOLD MAIR, and C. BORNHARDT (*Ber.*, 1911, **44**, 1169—1177).—When nitric oxide is passed into an ethereal solution of triphenylmethyl, the yellow coloration first produced rapidly changes into an intense bluish-green, and finally, in the course of one hour, into a pale yellow. The bluish-green coloration is doubtless due to the formation of *ω-nitrosotriphenylmethane*, $CPh_3\cdot NO$, which is then transformed into a colourless bisnitroso-compound. The substance is so unstable that its isolation was impossible. On evaporating the ethereal solution, it is decomposed into its constituents; small quantities of a colourless crystalline substance, m. p. 154—155°, seemingly formed by the combination of two molecules of triphenylmethyl and one of nitric oxide, are simultaneously produced. When treated with phenylhydrazine, the green solutions of triphenylnitrosomethane give off nitrogen.

A similar bluish-green coloration, evidently due to the formation of ω-nitrosotriphenylmethane and ω-chlorotriphenylmethane, is observed when nitrosyl chloride is passed into a solution of triphenylmethyl; by further introduction of nitrosyl chloride, the colour changes to deep yellowish-brown, owing to the formation of an additive compound of ω-chlorotriphenylmethane with nitrosyl chloride.

Triphenylmethyl interacts with nitrogen peroxide, yielding a mixture of *ω-nitrotriphenylmethane*, $CPh_3\cdot NO_2$, and *triphenylmethyl nitrite*, $CPh_3\cdot O\cdot NO$, the latter substance being produced in greater proportion.

The nitro-compound is best prepared by passing a current of carbon dioxide through liquid nitrogen peroxide, then through a hot glass tube in order to increase the proportion of the unimolecular form of nitrogen dioxide in the mixture, and finally into a concentrated ethereal solution of triphenylmethyl. It separates in the form of a colourless powder, consisting of flexible leaflets, m. p. 147°. It is decomposed by hot glacial acetic acid with the evolution of oxides of nitrogen, and, when warmed with concentrated sulphuric acid, gives a yellow coloration; when heated with phenol, it develops a brown colour.

Triphenylmethyl nitrite is contained in the ethereal filtrate from

the preparation of the preceding compound. It is more readily prepared by leading the nitrous gases, obtained by the addition of concentrated sulphuric acid to sodium nitrite and dried over phosphoric oxide, into a concentrated ethereal solution of triphenylcarbinol. It forms colourless crystals, m. p. 95—100°, which become red on exposure to moist air and give off oxides of nitrogen, with the formation of triphenylcarbinol; the same change is produced by warming the substance with glacial acetic acid. With phenol, it gives a brown coloration.

All attempts to prepare ω-nitrotriphenylmethane or triphenylmethyl nitrite by the interaction of ω-chlorotriphenylmethane and silver nitrite proved fruitless.

The authors find that triphenylmethyl is remarkably stable toward nascent hydrogen. When subjected to the prolonged action of aluminium amalgam in ethereal solution, it yields only a very small quantity of triphenylmethane, whilst, on treatment with sodium in the presence of water, it remains entirely unchanged. It is also different towards water; an ethereal solution of the substance, in the absence of air, undergoes no change even on prolonged contact with water.

The interaction of phenylhydrazine and triphenylmethyl leads to the formation of triphenylmethane and *s*-phenyltriphenylmethylhydrazine, $NHPh\cdot NH\cdot CPh_3$, which has m. p. 140°, and is oxidised with amyl nitrite to triphenylmethylazobenzene, m. p. 111° (compare Gomberg, Abstr., 1897, i, 40).

The behaviour of triphenylmethyl towards nascent carbon monoxide has also been investigated, by heating it with nickel carbonyl at 35—40°, but no combination occurred (compare Gomberg, Abstr., 1901, i, 77). Nickel carbonyl reacts with ω-chlorotriphenylmethane at the ordinary temperature, yielding nickel chloride and triphenylmethyl, with the evolution of carbon monoxide.

When triphenylcarbinol is heated at 185° with sodium, it yields a *sodium* derivative, which is obtained in the form of a white powder by removing unaltered carbinol with benzene or xylene. It decomposes at a high temperature, without melting, and, on treatment with water, is reconverted into the carbinol. Sodium has no action on triphenylcarbinol in xylene solution (compare Hemilian, this Journ., 1875, 152). F. B.

Mechanism of the Reaction in the Formation of Organo-magnesium Compounds. GEORGE L. STADNIKOFF (*Ber.*, 1911, 44, 1157—1160).—According to Tschelinzeff (Abstr., 1905, i, 40), oxonium compounds of the type $R_3O\cdot X$ (where X = halogen) are formed as intermediate products in the Grignard reaction. It should, therefore, be possible to find an ether, $R\cdot O\cdot R'$, the oxonium compound of which with an alkyl halide, $R\cdot X$, dissociates in two directions, according to the scheme: $R'X + R_2O \longleftarrow R_2R'O\cdot X \longrightarrow R'O\cdot R + RX$, and, in the presence of magnesium, gives rise to two magnesium compounds, $R\cdot MgX$ and $R'\cdot MgX$.

Evidence of the formation of two magnesium compounds has been

found by the author in the reaction between propyl iodide, triphenylmethyl ethyl ether, and magnesium.

These substances react in xylene solution, yielding magnesium propyl iodide and magnesium triphenylmethyl iodide, which separates out; on passing carbon dioxide into the mixture, butyric acid and triphenylmethane together with unchanged triphenylmethyl ethyl ether were obtained. F. B.

Tri-α-naphthylmethane. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1911, **44**, 1105—1107. Compare this vol., i, 277, 278).—The author's method of reduction with hydriodic and glacial acetic acids gives good, but not quantitative, results in the case of tri-α-naphthylcarbinol The chief product it *tri-α-naphthylmethane*, m. p. 191°. The hydrocarbon crystallises in glistening prisms with a faint bluish tinge, and melts in an atmosphere of carbon dioxide to a colourless liquid, with an intense blue fluorescence. The solutions of the substance also exhibit a blue fluorescence. By exposure to light, the hydrocarbon acquires a superficial brownish-yellow colour due to atmospheric oxidation. C. S.

Ortho-substituted Sulphinic Acids. MAX CLAASZ (*Annalen*, 1911, **380**, 303—316).—*o*-Acetylanilinesulphinic and *o*-nitrobenzenesulphinic acids have been prepared by reducing the corresponding sulphonic chlorides, in the former case with zinc dust and alcohol, and in the latter with the theoretical amount of stannous chloride and hydrochloric acid.

Unlike the majority of sulphinic acids these ortho-substituted acids are quite stable, and are not oxidised on exposure to the air; they are not so soluble in water as the corresponding sulphonic acids, but their sodium salts dissolve readily in both alcohol and water. With the exception of the *o*-nitrated acid they do not crystallise readily.

Sodium 4-bromoacetylaniline-2-sulphonate,

$$NHAc\cdot C_6H_3Br\cdot SO_3Na,H_2O,$$

obtained by acetylating Kreis's sodium 4-bromoaniline-2-sulphonate (Abstr., 1896, i, 48) with acetic anhydride at 170—180°, crystallises in colourless, felted needles. The *acid* is obtained by dissolving the sodium salt in ice-cold, concentrated hydrochloric acid, and washing with ether the crystals which are deposited after a time. It has m. p. 290—292° (decomp.). The *chloride*, $NHAc\cdot C_6H_3Br\cdot SO_2Cl$, has m. p. 121—122°, and the *sulphinic acid*, $NHAc\cdot C_6H_3Br\cdot SO_2H$, separates from boiling acetone as a crystalline powder, m. p. 138—140° (decomp.). *4-Bromo-1-aniline-2-sulphinic acid*, $NH_2\cdot C_6H_3Br\cdot SO_2H$, obtained by hydrolysing the acetyl derivative with 15% alcoholic potassium hydroxide solution, crystallises from pyridine in rosettes of needles, m. p. 160—163° (decomp.). The acid is insoluble in water, and the *sodium* salt, $C_6H_5O_2NSBrNa,2H_2O$, crystallises from alcohol. *Aniline-2-sulphinic acid*, $NH_2\cdot C_6H_4\cdot SO_2H$, cannot be obtained by reducing the bromo-acid, as the sulphinic group is reduced to the thiol group at the same time, but is formed when the somewhat unstable chloride of acetylaniline-2-sulphonic acid is reduced with zinc and then

hydrolysed with alcoholic potassium hydroxide. It crystallises from 50% alcohol on the addition of ethyl acetate, and decomposes at 141°.

Bromophenylglycinesulphonyl chloride, $CO_2H\cdot CH_2\cdot NH\cdot C_6H_3Br\cdot SO_2Cl$, prepared from the sodium hydrogen salt of the corresponding acid (Bradshaw, Abstr., 1906, i, 359), crystallises from benzene, decomposes at 158°, and on reduction yields 4-*bromo*-1-*glycylbenzene*-2-*sulphinic acid*, $CO_2H\cdot CH_2\cdot NH\cdot C_6H_3Br\cdot SO_2H$; a better yield of the same acid is obtained by condensing 4-bromoaniline-2-sulphinic acid with formaldehyde and potassium cyanide. It is almost insoluble in water, and decomposes at 219—221°. 4-*Bromomethylaniline*-2-*sulphonic acid*, $NHMe\cdot C_6H_3Br\cdot SO_3H$, obtained by methylating the sodium salt of the amino-acid with methyl iodide at 100°, crystallises in long, slender needles, moderately soluble in water. The corresponding *chloride* forms a viscid, reddish-brown oil, and when reduced yields a small amount of the *sulphinic acid*, $NHMe\cdot C_6H_3Br\cdot SO_2H$, as a colourless, crystalline powder, m. p. 166°. Aniline-2-sulphonic acid is quantitatively methylated by methyl iodide at 100° (compare Smyth, *Ber.*, 1874, 7, 1241).

o-Nitrobenzenesulphonyl chloride, prepared from the corresponding acid (Wohlfahrt, Abstr., 1903, i, 203), has m. p. 65°. It cannot be reduced by zinc dust or by sodium sulphide, but with the theoretical amount of stannous chloride and hydrochloric acid in alcoholic solution yields o-*nitrobenzenesulphinic acid*, $NO_2\cdot C_6H_4\cdot SO_2H$, which crystallises from concentrated solutions in glistening prisms, m. p. 134°. The *sodium* salt, $C_6H_4O_4NSNa$, crystallises from dilute alcohol in yellow plates, m. p. 123°. The *ethyl* ester, $C_8H_9O_4NS$, forms colourless, pointed plates, m. p. 58°. 1-*Chloro*-4-*nitrobenzenesulphinic acid*,

$$NO_2\cdot C_6H_3Cl\cdot SO_2H,$$

obtained from the corresponding sulphonyl chloride, crystallises from ether in colourless, compact prisms, m. p. 140°. The chlorine atom cannot be replaced by the amino-group (P. Fischer, Abstr., 1892, 331); with alcoholic ammonia at 120° no reaction takes place, and at 150—155°, *p*-chloronitrobenzene is obtained.

By the action of phosphorus pentachloride on sodium 4-nitroacetylaniline-2-sulphonate, the acetylamino-group is replaced by chlorine.

J. J. S.

p-Nitrosomethylethylaniline: a New Intermediate Product for the Manufacture of Dyes. John C. Cain (*7th Inter. Congr. App. Chem.*, 1909, Sect. IV B, 95).—p-*Nitrosomethylethylaniline* is prepared by treating methylethylaniline hydrochloride with nitrous acid; it crystallises in green plates, m. p. 66—67°. The *hydrochloride* forms yellow needles. The new compound can be used in the production of a number of dyes, and as an instance the author has prepared the corresponding methylene-blue from it. This substance, to which the name *methylene-blue M.E.* is given, dyes tannin-mordanted cotton in shades much greener than those produced by ordinary methylene-blue.

R. V. S.

Preparation of p-Hydroxy-β-phenylethylamine and its Derivatives. Farbenfabriken vorm. Friedr Bayer & Co. (D.R.-P. 230043).—A description is given of the preparation of *p*-methoxy-

β-phenylethylamine by methods already described (Rosenmund, Abstr., 1910, i, 106). The hydrochloride, which forms glistening leaflets, has m. p. 210° (Barger and Walpole, Trans., 1909, **95**, 1724, give 206°). *p*-Hydroxyphenylethylamine is obtained by the reduction of *p*-hydroxyphenylacetaldehyde-*p*-nitrophenylhydrazone (compare Langheld, Abstr., 1909, i, 557). F. M. G. M.

p-**Aminostilbene.** PAUL PFEIFFER and S. SERGIEWSKAJA (*Ber.*, 1911, **44**, 1107—1112).—By heating a mixture of *p*-nitrophenylacetic acid and benzaldehyde at 205°, Walther and Wetzlich obtained *p*-nitrostilbene-μ-carboxylic acid, but were unable to eliminate carbon dioxide from the acid. The author finds that this can be accomplished by heating the acid with piperidine at about 160°. The p-*nitrostilbene*, $CHPh{:}CH{\cdot}C_6H_4{\cdot}NO_2$, which is thus produced and which can also be prepared by heating a mixture of *p*-nitrophenylacetic acid, benzaldehyde, and piperidine at 150—160°, has m. p. 155°, crystallises in yellow needles, and forms a *dichloride*, m. p. 152°, and *dibromide*, m. p. 198°. It is reduced by stannous chloride and hydrogen chloride in glacial acetic acid, yielding p-*aminostilbene*, m. p. 151—152°, which is colourless, but becomes yellow in light. The base forms a *hydrochloride*, $C_{14}H_{13}N,HCl$, m. p. 245—250° (decomp.), an *acetyl* derivative, m. p. 225°, and a *benzoyl* derivative, m. p. 244—245°. C. S.

Preparation of Carbonic Acid Esters. CHEMISCHE FABRIK LADENBURG (D.R.-P. 230827).—An account of experiments which resulted in the isolation of carbonic acid esters of the general formulæ:

$CR''(OR)_2$	$C(NHR)_2(OR)_2$	$NHR{\cdot}C({:}NR){\cdot}OR$	CSR'_2
(I.)	(II.)	(III.)	(IV.)

where R″ is a bivalent organic residue or sulphur, R′ a univalent organic radicle, and R an aryl or substituted aryl group.

Diphenyl thioncarbonate, $CS(OPh)_2$, m. p. 101°, was prepared by heating together lead oxide, phenol, and carbon disulphide.

*Triphenyl*iso*carbamide*, $NPh{:}C(OPh){\cdot}NHPh$, colourless leaflets, m. p. 99°, was obtained by heating diphenylthiocarbamide with lead phenoxide.

Diphenyl allyliminocarbonate, $C_3H_5{\cdot}N{:}C(OPh)_2$, odourless and tasteless, greyish-white needles, m. p. 82°, was prepared in analogous manner with allylthiocarbimide, whilst phenylthiocarbimide yielded diphenyl phenyliminocarbonate, m. p. 134°.

p-*Dihydroxydiphenylthiocarbamide*, $CS(NH{\cdot}C_6H_4{\cdot}OH)_2$, colourless tablets which become purple on exposure, m. p. about 225° (decomp.), was prepared by boiling *p*-aminophenol with carbon disulphide in alcoholic solution; when heated at 120° with lead phenoxide it yielded the unstable, crystalline compound,

$$OH{\cdot}C_6H_4{\cdot}NH{\cdot}C(OPh){:}N{\cdot}C_6H_4{\cdot}OH.$$

F. M. G. M.

Preparation of *m*-Tolyl ortho-Oxalate. RÜTGERSWERKE-AKTIENGESELLSCHAFT and CURT GEUTSCH (D.R.-P. 229143).—When

m-cresol (2 mols.) and anhydrous oxalic acid (1 mol.) are mixed together the mass solidifies, yielding m-*tolyl ortho-oxalate*,

$$C_7H_7\cdot O\cdot C(OH)_2\cdot C(OH)_2\cdot O\cdot C_7H_7,$$

in which the powerful disinfectant properties of *m*-cresol are enhanced; at 51° it decomposes into its generators. F. M. G. M.

Chlorination of α-Naphthol. Hermann Kast (*Ber.*, 1911, **44**, 1337. Compare Reissert, this vol., i, 368).—By the action of sulphuryl chloride diluted with chloroform on α-naphthol dissolved in boiling chloroform, 4-chloro-α-naphthol, crystallising in long needles, m. p. 120—121°, is obtained in good yield. In the cold the yield is smaller, and a number of soluble by-products are formed. E. F. A.

Nitrosonaphthols or Naphthaquinoneoximes. Carl H. Sluiter (*Ber.*, 1911, **44**, 1327—1332. Compare Abstr., 1906, i, 255).—It is shown by conductivity measurements in mixtures of acetone and water, and by determinations of the molecular weight by the boiling point method in acetone and alcoholic solution that the three nitrosonaphthols have the following structure.

Brown nitrosonaphthol, $C_6H_4<\begin{array}{l}C(:N\cdot OH)\cdot CO\\ CH{=\!=\!=}CH\end{array}$, is an oxime, but the salts are nitroso-derivatives, $C_6H_4<\begin{array}{l}C(NO):C(OMe)\\ CH{=\!=}CH\end{array}$.

Yellow nitrosonaphthol, $C_6H_4<\begin{array}{l}CO\cdot C:N\cdot OH\\ CH:CH\end{array}$, is an oxime, and its salts are also derived from the same formula.

Colourless nitrosonaphthol, $C_6H_4<\begin{array}{l}C(OH):CH\\ C(NO):CH\end{array}$, is a nitroso-compound, but the salts are derived from the oxime,

$$C_6H_4<\begin{array}{l}CO{-\!-\!-\!-}CH\\ C(:N\cdot OMe)\cdot CH\end{array}.$$

These conclusions are in agreement with the colour changes of the nitrosonaphthols and their salts. The solid, colourless nitrosonaphthol is dimolecular, but it is dissociated to green, single molecules in solution. E. F. A.

Action of Bromine and Chlorine on Phenols. Substitution Products. ψ-Bromides and ψ-Chlorides. XXV. A ψ-Bromide from *p*-Cresol containing Sulphur and its Transformations. Theodor Zincke, W. Frohneberg, and J. Kempf (*Annalen*, 1911, **381**, 28—51).—2 : 5-Dibromo-3-methylthiol-*p*-cresol ψ-bromide (this vol., i, 288) contains a reactive bromine atom which is readily replacable by hydroxy-, methoxy-, and ethoxy-groups. The view that the compound contains either of the groupings $\cdot SBr:CH_2$ or $S\cdot CH_2Br$ is shown to be untenable, since neither the perbromide derived from *o*-cresol nor the perbromide from the *p*-cresyl methyl ether (this vol., i, 198) yields a similar derivative. The constitution already suggested for the ψ-bromide is confirmed by its behaviour towards an acetic acid solution of nitric acid; the sulphur group is removed and replaced by a nitro-group, but all three bromine atoms are left

intact. The resulting nitro-compound reacts as a ψ-bromide and yields a methoxy-derivative by the replacement of one bromine by methoxyl; this derivative is identical with the product prepared by the action of nitric acid on the methoxy-compound derived from the original ψ-bromide, namely, $NO_2{\cdot}C_6HBr_2(NO_2){\cdot}CH_2{\cdot}OMe$.

It is suggested that the ψ-bromide is formed from the perbromide by the following series of reactions:

$$CH{<}\begin{smallmatrix}CMe{-}CBr\\CBr{:}C(OH)\end{smallmatrix}{>}C{\cdot}SMeBr_2 \longrightarrow CH{<}\begin{smallmatrix}CMe{:}CBr\\CBr{-}CO\end{smallmatrix}{>}C{:}SMeBr \longrightarrow$$

$$CH{<}\begin{smallmatrix}CMeBr{\cdot}CBr\\CBr{-\!-}CO\end{smallmatrix}{>}C{\cdot}SMe \longrightarrow CH{<}\begin{smallmatrix}C(CH_2Br){:}CBr\\CBr{-\!-}C(OH)\end{smallmatrix}{>}CSMe$$

and that this type of reaction is characteristic of *o*-alkylthiolphenols.

The simplest method of obtaining the ψ-bromide is by the action of potassium acetate on the perbromide in the presence of glacial acetic acid. When prepared by shaking the perbromide with water and ether, it is advisable to use a large volume of water, as otherwise much sulphoxide is formed. When treated with normal sodium hydroxide solution, the ψ-bromide yields a dark green sodium salt, which yields a sparingly soluble yellow product when acidified. With pyridine the ψ-bromide yields a *pyridinium* salt, which is decomposed by water, and when reduced the bromide yields 2 : 5-dibromo-3-methylthiol-*p*-cresol.

The *acetyl* derivative of the ψ-bromide, $OAc{\cdot}C_6HBr_2(SMe){\cdot}CH_2Br$, crystallises from methyl alcohol in colourless cubes, m. p. 136°.

2 : 5-*Dibromo-4-hydroxy-3-methylthiolbenzyl alcohol*,

$$OH{\cdot}C_6HBr_2(SMe){\cdot}CH_2{\cdot}OH,$$

prepared by the action of water on an acetone solution of the ψ-bromide, crystallises in clear yellow, glistening plates, m. p. 125—126°, and is transformed into the ψ-bromide by a glacial acetic acid solution of hydrogen bromide. The corresponding *methyl ether*, $OH{\cdot}C_6HBr_2(SMe){\cdot}CH_2{\cdot}OMe$, forms small, colourless needles, m. p. 81—82°, and with nitric acid yields 2 : 5-*dibromo-3-nitro-4-hydroxybenzyl methyl ether*, $OH{\cdot}C_6HBr_2(NO_2){\cdot}CH_2{\cdot}OMe$, which crystallises from light petroleum in long, yellow needles, m. p. 120—121°. 2 : 5-*Dibromo-4-hydroxy-3-methylthiolbenzyl acetate*,

$$OH{\cdot}C_6HBr_2(SMe){\cdot}CH_2{\cdot}OAc,$$

crystallises in stout, colourless needles, m. p. 137°. It does not behave as a phenol, and probably has a quinonoid structure; with acetic anhydride it yields the *diacetyl* derivative,

$$OAc{\cdot}C_6HBr_2(SMe){\cdot}CH_2{\cdot}OAc,$$

in the form of small, colourless needles, m. p. 131°.

2 : 5-*Dibromo-3-nitro*-p-*cresol* ψ-*bromide*, $OH{\cdot}C_6HBr_2(NO_2){\cdot}CH_2Br$, crystallises from light petroleum in brilliant yellow needles, m. p. 118—119°.

The black quinone (this vol., i, 288) obtained by the action of solid sodium acetate on an ethereal solution of 2 : 5-dibromo-3-methylthiol-*p*-cresol ψ-bromide is regarded as 2 : 5 : 2′ : 5′-*tetrabromo*-3 : 3′-*dimethylthiolstilbene* - p - *quinone*, $O{:}C_6HBr_2(SMe){:}CH{\cdot}CH{:}C_6HBr_2(SMe){:}O$ (compare Zincke and Fries, Abstr., 1903, i, 178). It forms a deep

black powder, m. p. 240° (decomp.), and is practically insoluble in the usual solvents. With acetic acid, acetic anhydride, and a little sulphuric acid the quinone yields 2 : 5 : 2′ : 5′-*tetrabromo*-4 : 4′-*diacetoxy*-3 : 3′-*dimethylthiolhydrobenzoin diacetate*,

$$C_2H_2(OAc)_2\cdot[C_6HBr_2\cdot(SMe)OAc]_2,$$

which forms stout, colourless crystals, m. p. 236°. *Tetrabromodihydroxydimethylthiolhydrobenzoin dimethyl ether*,

$$C_2H_2(OMe)_2[C_6HBr_2(SMe)\cdot OH]_2,$$

obtained by warming the quinone with methyl alcohol and $2N$-sodium hydroxide solution, forms glistening, colourless, rhombic crystals, m. p. 182°, and yields a *diacetyl* derivative, $C_{22}H_{22}O_6S_2Br_4$, m. p. 220—222° (decomp.). When reduced with stannous chloride and a glacial acetic acid solution of hydrogen chloride, the quinone yields 2 : 5 : 2′ : 5′-*tetrabromo*-4 : 4′-*dihydroxy*-3 : 3′-*dimethylthiolstilbene*, $C_2H_2[C_6HBr_2(SMe)\cdot OH]_2$ as colourless, glistening plates, m. p. 245°, which is readily oxidised to the quinone. The *diacetyl* derivative, $C_{20}H_{16}O_4S_2Br_4$, forms colourless needles, m. p. above 280°. When suspended in chloroform and treated with hydrogen bromide, the quinone yields the additive compound, *tetrabromodihydroxydimethylthiolstilbene dibromide*, $C_{16}H_{12}O_2S_2Br_6$, in the form of small, colourless needles, m. p. 205° (decomp.), which can be readily transformed back into the quinone.

In the preparation of the quinone from the ψ-bromide an appreciable amount of 2 : 5 : 2′ : 5′-*tetrabromo*-4 : 4′-*dihydroxy*-3 : 3′-*dimethylthioldibenzyl*, $C_2H_4[C_6HBr_2(SMe)\cdot OH]_2$, is obtained. It crystallises from glacial acetic acid in thin, glistening plates and needles, m. p. 202°, and yields a *diacetyl* derivative, $C_{20}H_{18}O_4S_2Br_4$, in the form of colourless plates, m. p. 219°. With nitric acid, the dibenzyl derivative yields a *nitro*-compound, $C_{14}H_8O_6N_2Br_4$, which crystallises from tetrachloroethane in small, yellow prisms, m. p. above 260° (decomp.). The dibenzyl derivative also yields a *perbromide*,

$$C_2H_4[C_6HBr_2(SMeBr_2)_2\cdot OH]_2,$$

which decomposes at about 150°. This perbromide reacts with $0{\cdot}5N$-sodium hydroxide solution in the presence of chloroform, yielding a black quinone very similar to the one described above.

In the preparation of the quinone and the dibenzyl derivative from the ψ-bromide, it is probable that an unstable methylenequinone is first formed, and that this is partly oxidised to the quinone and partly reduced to the dibenzyl-derivative. J. J. S.

Preparation of Nitrophenyl Mercaptans. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 228868. Compare Abstr., 1908, i, 631).—Satisfactory yields of nitrophenyl mercaptans are readily obtained when an alcoholic alkaline solution (8 to 10 parts NaOH) of the corresponding dinitrodiaryl disulphide (1 part) is heated with half an equivalent of sodium hydrosulphide on a water-bath.

With *pp′*-dinitrophenyl disulphide, glistening, golden-yellow leaflets of *sodium* p-*nitrothiophenoxide* separate from the reaction mixture.

F. M. G. M.

Phenol-*m*-sulphonic Acid and its Isolation. Its Non-formation from Phenol and Sulphuric Acid. JULIUS OBERMILLER (*Annalen*, 1911, 381, 114—122).—Phenol-*m*-sulphonic acid is best prepared by diazotising *m*-aminobenzenesulphonic acid and boiling with water containing 2% sulphuric acid (compare Berndsen, this Journ., 1875, 1028; Kreis, Abstr., 1896, i, 48). It is not readily isolated as its sodium salt, as this is readily soluble, but the *magnesium* salt, $(OH\cdot C_6H_4\cdot SO_3)_2Mg,6H_2O$, crystallises in long, brittle plates. Its saturated aqueous solution has D 1·190 at 15—20°.

The barium, strontium, calcium, lead, copper, aluminium, and potassium salts do not crystallise at all well. Their solutions are neutral to Congo-red, but slightly acid to litmus. The *sodium* salt crystallises in broad plates, and the *zinc* salt in thin, flat, pointed prisms.

The following salts of the type $MO\cdot C_6H_4\cdot SO_3M$ are stable:—sodium, potassium, calcium, strontium, and barium, but they do not crystallise. The corresponding magnesium, zinc, copper, and aluminium salt are hydrolysed by hot water, yielding precipitates of the hydroxides. A basic *lead* salt can be used for the isolation of the acid, and is best obtained by treating the crude sodium salt with lead acetate (0·5 mol.) and pure lead hydroxide (1·5 mol. obtained from lead acetate) in the form of a cream and much water. This basic salt yields the ordinary lead salt on the addition of sulphuric acid, and from this the other salts can be prepared.

A method has been worked out for isolating the meta-acid from a mixture of the ortho-, meta-, and para-acids. The para-acid can be removed in the form of its characteristic strontium salt, the ortho- and 2:4-acids can be removed by conversion into basic barium salts and addition of alcohol, and the meta-acid isolated from the final mother liquor as its characteristic magnesium salt. By means of this method it is shown that no trace of the meta-acid is formed by the action of sulphuric acid on phenol either at 15—20° or at 90—100° when 1·5 gram-mols. of sulphuric acid are used.

The sulphonic acid group of the meta-acid is not removed by the action of bromine (bromide and bromate mixture). J. J. S.

Action of Magnesium *p*-(or *o*-)Tolyl Bromide on *sym*.-Dibromomethyl Ether. Preparation and Properties of Xylyl Ether. N. PAWLOWSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 214—218).—p-*Xylyl ether*, $(C_6H_4Me\cdot CH_2)_2O$, prepared by the interaction of *p*-bromotoluene, magnesium, and *s*-dibromomethyl ether, crystallises in white, shining scales, greasy to the touch, m. p. 61—62°, b. p. 310—311°, and has the normal molecular weight in freezing benzene or boiling ether.

o-*Xylyl ether*, $(C_6H_4Me\cdot CH_2)_2O$, prepared in a similar manner to its isomeride, is a colourless, oily liquid, b. p. 201—203°/26 mm., $n_D^{19\cdot8}$ 1·55784, and has the normal molecular weight in freezing benzene or boiling ether.

When treated with hydrobromic acid, *p*- and *o*-xylyl ethers yield *p*- and *o*-xylyl bromides respectively.

p-*Xylyl iodide* C_8H_9I, prepared by the action of hydriodic acid on

p-xylyl ether, forms long, transparent needles, m. p. 45·5—46·5°, and o-*xylyl iodide*, similarly prepared, long, transparent needles, m. p. 34°.
T. H. P.

Generalisation of the Formation of Mixed Organo-magnesium Compounds with Oxygenated Compounds. BERNARDO ODDO (*Gazzetta*, 1911, 41, i, 273—294).—It was shown by Tschelinzeff (Abstr., 1904, i, 559) that tertiary cyclic amines, especially dimethylaniline, can replace ether in the preparation of Grignard's compounds, also (Abstr., 1905, i, 40) that the ethereal oxygen and the tertiary nitrogen act catalytically, it being possible to prepare mixed organo-magnesium compounds in presence of neutral solvents, such as benzene and toluene, containing a trace of ether or dimethylaniline.

The aim of the present work was to ascertain whether, by operating in presence of an indifferent solvent absolutely free from all trace of ether or tertiary base, it is possible to generalise the process of formation of organo-magnesium compounds. For this purpose a compound containing a carbonyl oxygen atom was employed, since the researches of von Baeyer and Villiger have shown that such oxygen appears capable of giving salts, that is, of displaying two supplementary valencies. It is found that the reaction proceeds according to the following equations: $R\cdot CO\cdot R' + CH_3I = CRR'{:}OIMe$; $CRR'{:}OIMe + Mg = CRR'{:}OI\cdot MgMe$; $CRR'{:}OI\cdot MgMe + R\cdot CO\cdot R' = CRR'Me\cdot O\cdot MgI + R\cdot CO\cdot R'$; $CRR'Me\cdot O\cdot MgI + H_2O = CRR'Me\cdot OH + MgI\cdot OH$. The reaction takes place, not only with aldehydes and ketones, but also with esters, with compounds, such as β-naphthol, which exhibit a tendency to the formation of a carbonyl oxygen, and with compounds in which oxygen is doubly linked to an element other than carbon, such as nitro-derivatives; in all instances, the same compounds are obtained as are given by the action of Grignard's reagent. Under the conditions employed, magnesium exerts no action on an alkyl iodide alone. The benzene used as solvent was absolutely free from thiophen.

[With G. DEL ROSSO.]—Benzaldehyde, magnesium, and ethyl iodide give (1) phenylethylcarbinol; (2) α-phenyl-Δ^{α}-propylene,

$$CHPh{:}CHMe,$$

formed by the loss of water from phenylethylcarbinol, and (3) the *ether*, $(CHPhEt)_2O$, which is a dense liquid, b. p. 222°/30 mm., and crystallising in white needles, m. p. 82°.

Benzaldehyde, magnesium, and propyl iodide yield: (1) phenylpropylcarbinol (compare Klages, Abstr., 1904, i, 567); (2) *phenylpropylcarbinyl ether*, $(CHPhPr^{\alpha})_2O$, which forms acicular crystals, m. p. 131°, b. p. 208—210°/30 mm., has the normal molecular weight in freezing benzene, and can also be obtained by boiling phenylpropylcarbinol with a crystal of stannous chloride; (3) a small proportion of butenylbenzene.

p-Tolualdehyde, magnesium, and ethyl iodide give: (1) *p*-tolylethylcarbinol (compare Klages, Abstr., 1904, i, 27); (2) a *dimeride* of p-*tolualdehyde*, m. p. 130°, and (3) *p*-xylyl alcohol.

With paraldehyde, magnesium, and ethyl iodide, the reaction pro-

ceeds exceptionally readily, the products being : (1) β-hydroxybutane and (2) Δ^{α}- and Δ^{β}-butylenes. The facility with which the action takes place depends on the presence of the molecule :

$$CHMe{<}\begin{matrix}O{\cdot}CHMe\\O{\cdot}CHMe\end{matrix}{>}O,$$

the symmetrical ring organo-magnesium compound formed being decomposed by the heat developed during its formation into simple molecules of the type $CHMeR{\cdot}O{\cdot}MgX$.

Acetone, magnesium, and ethyl iodide yield dimethylethylcarbinol. Treatment of the products of the reaction with acetyl chloride gave, not the acetyl derivative of the alcohol, but an unstable *liquid*, b. p. 54°/30 mm., probably of the structure $CMe_2Et{\cdot}OI$.

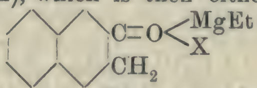
Acetone, magnesium, and methyl iodide give trimethylcarbinol.

Methyl benzoate, magnesium, and ethyl iodide yield : (1) phenyldiethylcarbinol, thus :

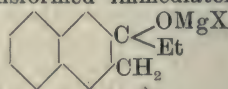
$$2R{\cdot}MgX + R'{\cdot}CO_2Me = OMe{\cdot}MgX + CR_2R'{\cdot}O{\cdot}MgX,$$

the last product giving the tertiary alcohol on treatment with water ; (2) γ-phenyl-Δ^{β}-amylene (compare Klages, Abstr., 1904, i, 27).

In the reaction between β-naphthol, magnesium, and ethyl iodide, the naphthol seems to react in its ketonic form, giving the compound (I), which is then either transformed immediately into (II),



(I.)



(II.) ,

or, being in presence of naphthol with a hydroxylic function, yields ethane and the iodomagnesium derivative of β-naphthol. Nitrobenzene, magnesium, and ethyl iodide yield phenylethylamine and azobenzene. T. H. P.

Action of Zinc on a Mixture of 1-Methyl*cyclo*hexan-3-one and Allyl Iodide. MICHAEL SAYTZEFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 345—349).—1-*Methyl-3-allyl*cyclo*hexen-3-ol*,

$$CH_2{<}\begin{matrix}CHMe{\cdot}CH_2\\CH_2{-}{-}CH_2\end{matrix}{>}C(OH){\cdot}C_3H_5,$$

prepared by the action of zinc on a mixture of 1-methyl*cyclo*hexan-3-one and allyl iodide in ethereal solution, is a mobile liquid, b. p. 206—209°, D_0^0 0·92244, D_{20}^{20} 0·91343. When oxidised with permanganate (1 atom of oxygen per mol. of alcohol) it yields the white, crystalline, trihydric *alcohol*, $CH_2{<}\begin{matrix}CHMe{\cdot}CH_2\\CH_2{-}{-}CH_2\end{matrix}{>}C(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, whilst with 5% permanganate solution (4O per mol. of alcohol) it gives the *acid*, $CH_2{<}\begin{matrix}CHMe{\cdot}CH_2\\CH_2{-}{-}CH_2\end{matrix}{>}C(OH){\cdot}CH_2{\cdot}CO_2H$, as a viscous, dark yellow liquid ; the *calcium* salt was prepared. T. H. P.

Action of Magnesium on a Mixture of Allyl Bromide and Benzaldehyde. Synthesis of Phenylallylcarbinol. D. KLIMENKO (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 212—213).—The action of magnesium on allyl bromide and benzaldehyde (compare Javorsky, Abstr., 1908, i, 753) yields phenylallylcarbinol, b. p. 126—127°/

24 mm., $D_4^{25\cdot6}$ 1·0161, n_D 1·53251 (compare Fournier, Abstr., 1894, i, 19). When oxidised with permanganate (0·5—4%) it yields the quantitative proportion of benzoic acid and traces of a neutral syrupy product (? glycerol). T. H. P.

Action of Magnesium on a Mixture of Allyl Bromide and Piperonal. N. D. KORJUKIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 208—211).—*δ-Methylenedioxyphenyl-Δ^α-buten-δ-ol*,

$$CH_2<^O_O>C_6H_3\cdot CH(OH)\cdot CH_2\cdot CH:CH_2,$$

obtained by the interaction of magnesium, allyl bromide, and piperonal, is a viscous liquid, b. p. 166—167°/23·5 mm., $D_4^{23\cdot6}$ 1·2016, $n_D^{23\cdot6}$ 1·55489, having the normal molecular weight in freezing benzene and in boiling ether.

On oxidation with permanganate it yields piperonylic acid (compare Jobst and Hesse, Abstr., 1880, 325). T. H. P.

Preparation of *o*-Chlorobenzotrichloride. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 229873).—When sodium *o*-chlorobenzylsulphonate is treated with phosphorus pentachloride, it yields *o-chlorobenzylsulphonyl chloride*, colourless crystals, m. p. 56—58°; this, on treatment with chlorine gas at a temperature of 150—180° until the evolution of hydrogen chloride ceases and subsequent distillation in a vacuum, yields *o-chlorobenzotrichloride*, b. p. 115—118°/5·6 mm. F. M. G. M.

The Influence of the Composition and Structure of Organic Acids on the Stability of their Carboxyl Group. PAUL N. RAIKOFF and P. TISCHKOFF (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI, 91—96. Compare Cazeneuve, Abstr., 1892, 1332; Raikoff and Tischkoff, Abstr., 1906, i, 83).—A flask containing 40 c.c. of phosphoric acid, D 1·78, is heated to 200°, cooled to 50°, and 1/30 gram-equivalent of the acid to be studied is introduced. A reflux condenser is then attached, connected with a graduated tube provided with two taps and dipping into mercury. The flask is heated in an oil-bath, and the volume of gas is read off at temperatures rising by 10° from 100° to 190°, then at 195° and 200°. The total volume of gas is finally measured after expulsion by mercury. The proportions of carbon dioxide and monoxide are determined by analysis. A table in the paper contains the results from sixty-five organic acids.

The stability of the carboxyl group in benzoic acid is generally reduced by substitution in the ring. Substitution in one or both meta-positions is almost without influence on the stability, whilst ortho- and para-substituents exert an influence dependent on the nature of the radicle. The very active groups include OH, NH_2, OMe, COMe; the moderately active groups I, IO, Me, NO_2, and the inactive H, Cl, Br, CN, CO_2H, Ph, $C_6H_4\cdot CO_2H$, $C(C_6H_4\cdot OH)_2$, Bz, $CO\cdot C_{10}H_7$. The effect of two groups is shown by a comparison of seven substituted salicylic acids. C. H D.

Alkylation of Aromatic Amino-acids. V. 3-Amino-2:4-dimethylbenzoic Acid. HENRY L. WHEELER and CHARLES HOFFMAN (*Amer. Chem. J.*, 1911, **45**, 436—445).—It has been shown in an earlier paper (Abstr., 1910, i, 666) that 2-aminomesitylenic acid on alkylation yields the diethylamino-derivative (30 parts), the ethylamino-derivative (10 parts), and the ester (1 part), whereas 4-aminomesitylenic acid gives the ester only. In view of these results, a study has been made of the behaviour of 3-amino-2 : 4-dimethylbenzoic acid, which, like 4-aminomesitylenic acid, has the amino-group situated between two methyl groups, and it has been found that this acid also yields the ester as the chief product of alkylation.

3-*Nitro*-5-*amino*-2 : 4-*dimethylbenzoic acid*, m. p. 251°, obtained by reducing 3 : 5-dinitro-2 : 4-dimethylbenzoic acid (Frey and Horowitz, Abstr., 1891, 566) with ammonium sulphide, crystallises in straw-coloured prisms; its *hydrochloride* has m. p. 250° (decomp.), and its *acetyl* derivative, m. p. 247°, forms colourless needles. When this acid is diazotised and treated with alcohol, it is converted into 3-nitro-2 : 4-dimethylbenzoic acid, m. p. 179° (not 135° as stated by Clausius, Abstr., 1890, 980), which forms light brown prisms; its *amide*, m. p. 138°, crystallises in plates. 3-*Amino*-2 : 4-*dimethylbenzoic acid*, m. p. 146°, obtained by reducing the nitro-acid with ferrous hydroxide, forms needles or prisms, and, when distilled with calcium oxide, yields *vic.*-*m*-xylidine. The aqueous and alcoholic solutions of the acid have a green fluorescence. The *acetyl* derivative, m. p. 243° (decomp.), crystallises in needles. 3-*Iodo*-2 : 4-*dimethylbenzoic acid*, m. p. 167°, obtained by the action of potassium iodide on the diazotisation product of 3-amino-2 : 4-dimethylbenzoic acid, forms needle-like prisms. When 3-amino-2 : 4-dimethylbenzoic acid is heated with ethyl iodide, ethyl alcohol, and potassium hydroxide, the *ethyl* ester is obtained as an oil. On treating the acid with methyl iodide under similar conditions, the *methyl* ester is produced, together with a small quantity of 3-methylamino-2 : 4-dimethylbenzoic acid.

When 2 : 4 : 6-tribromo-3-aminobenzoic acid is heated with methyl iodide in presence of potassium hydroxide and methyl alcohol, the *methyl* ester, m. p. 93—94°, is obtained as the only product of the reaction and forms colourless needles.

It has been shown (this vol., i, 50) that the acid formerly described as 4-amino-*m*-toluic acid (Abstr., 1910, i, 666) is really 2-amino-*m*-toluic acid. This is now confirmed by the observation that when the acid is distilled with calcium oxide it yields *o*-toluidine. E. G.

Turmeric Oil. IV. Synthesis of α-*p*-Tolyl-α-methylbutyric Acid. HANS RUPE and J. BÜRGIN (*Ber.*, 1911, **44**, 1218—1225. Compare this vol., i, 69, 293).—α-*p*-Tolyl-α-methylbutyric acid, the second of the three acids (*loc. cit.*), one of which the authors believe to be identical with curcumic acid, has now been synthesised, but, like γ-*p*-tolylvaleric acid, it is not identical with, although very similar to, curcumic acid.

In the earlier attempts to synthesise α-*p*-tolyl-α-methylbutyric acid, the authors used p-*tolylmethylethylcarbinol*, $C_{11}H_{16}O$, b. p. 108·5—109°/

10 mm., obtained in the usual way from magnesium *p*-tolyl bromide and methyl ethyl ketone, but abandoned the process owing to the difficulty of converting the alcohol into its chloride and making the latter react with magnesium.

Subsequently *a*-*p*-tolyl-*a*-methylbutyric acid, $C_{12}H_{16}O_2$, was obtained from ethyl *a*-bromo-*a*-methylbutyrate, toluene, and freshly distilled aluminium bromide by Wallach's process (Abstr., 1900, i, 229). It has the same b. p., 171°/13 mm., as curcumic acid, but could not be obtained in the solid state; moreover, the calcium salts of the two acids differ in solubility, and the synthetic acid, by oxidation with 4% potassium permanganate and sodium carbonate at 0°, yields products different from those obtained from the oxidation of curcumic acid.

p-Tolylmethylethylcarbinol is converted by boiling acetic anhydride into *β-p-tolyl-Δ^{β}-butylene*, $C_6H_4Me\cdot CMe\colon CHMe$, b. p. 93·5—94°/10 mm., the constitution of which is proved by the production of *p*-tolyl methyl ketone by oxidation by alkaline 2% potassium permanganate. A bimolecular *polymeride*, $(C_{11}H_{14})_2$, b. p. 201—202°/9 mm., is obtained when the carbinol is dehydrated by 95% formic acid. C. S.

Action of Light on Esters of *a*-Cyanocinnamylideneacetic Acid. MARIE REIMER (*Amer. Chem. J.*, 1911, **45**, 417—436).—During the course of some work on the behaviour of certain esters of cinnamylideneacetic and cinnamylidenemalonic acids towards Grignard's reagent, it was observed that the esters were decomposed by light. The nature of these changes is being investigated, and an account is now given of the action of light on esters of *a*-cyanocinnamylideneacetic acid.

Riiber (Abstr., 1902, i, 617) has shown that cinnamylidenemalonic acid is converted by the action of sunlight into diphenyltetramethylenebismethylenemalonic acid, and Macleod (Abstr., 1910, i, 846) has found that a similar change takes place in the case of *a*-methylcinnamylideneacetic acid.

Methyl a-cyanocinnamylideneacetate, m. p. 145°, can be readily prepared by the condensation of methyl cyanoacetate with cinnamaldehyde in presence of sodium methoxide, and forms yellow crystals. When exposed to sunlight it rapidly changes to a white substance, which separates from a mixture of acetone and light petroleum in the form of transparent crystals, and on oxidation with potassium permanganate yields truxillic, benzoic, and oxalic acids. The compound is therefore *methyl* 1 : 3-*diphenyl*cyclo*butane* 2 : 4-*di-a-cyanoacrylate*,

$$CO_2Me\cdot C(CN)\colon CH\cdot CH{<}{}^{CHPh}_{CHPh}{>}CH\cdot CH\colon C(CN)\cdot CO_2Me;$$

it has m. p. 172·5°, is but little affected by bromine, and when distilled under 20 mm. pressure is re-converted into methy *a*-cyanocinnamylideneacetate.

Ethyl *a*-cyanocinnamylideneacetate (Bechert, Abstr., 1894, i, 488) behaves quite differently from the methyl ester, and is converted by light into a *compound*, m. p. 166°, which probably has the structure $CO_2Et\cdot C(CN)\colon CH\cdot CH_2\cdot CHPh\cdot C(CHPh)\cdot CH\colon C(CN)\cdot CO_2Et$; it forms white crystals and, when distilled under reduced pressure, yields a mixture of stable and unstable ethyl *a*-cyanocinnamylideneacetates.

On oxidation with potassium permanganate, benzaldehyde and benzoic acid are produced together with traces of an *acid*, $C_{11}H_{10}O_5$, m. p. about 179°. When oxidised with potassium dichromate, benzoic acid is formed together with an *acid*, $C_{18}H_{16}O_4$, m. p. 185°, which forms white, slender needles, and gives a *methyl* ester, m. p. 132°, crystallising in transparent rhombic crystals. When the compound (m. p. 166°) is treated at 0° with a solution of bromine in chloroform, a *dibromide*, m. p. 125—127°, is obtained, which forms white, lustrous crystals. In one experiment in which much less than the calculated quantity of bromine was used, *ethyl* 1 : 3-*diphenyl*cyclo*butane* 2 : 4-*di-a-cyanoacrylate*,

$$CO_2Et\cdot C(CN)\colon CH\cdot CH<{}^{CHPh}_{CHPh}>CH\cdot CH\colon C(CN)\cdot CO_2Et,$$

m. p. 128°, was produced, which forms colourless crystals and, on oxidation, behaves in the same way as the corresponding methyl ester.

The difference in the behaviour of methyl and ethyl α-cyanocinnamylideneacetates on exposure to light is probably due to a difference in their configuration, the former being an unstable, and the latter a stable form. An unstable modification of ethyl α-cyanocinnamylideneacetate has been obtained from the methyl ester by the action of potassium ethoxide on its solution in absolute alcohol (compare Pfannl, Abstr., 1910, i, 480); it has the same m. p. (113°) as the stable form, but is much less soluble in alcohol than the latter. It is affected by light in the same way as the methyl ester from which it is produced, being rapidly converted into ethyl diphenyl*cyclo*butanedicyanoacrylate. E. G.

Stilbene-*o*-carboxylic Acids. PAUL PFEIFFER and K. MATTON (*Ber.*, 1911, **44**, 1113—1124).—The authors have prepared derivatives of stilbene-*o*-carboxylic acids, partly to extend the knowledge of such substances, partly for stereochemical examination. A mixture of phthalonic acid, a little piperidine, and 2 : 4-dinitrotoluene, *o*-nitro-*p*-toluonitrile, or *p*-nitro-*o*-toluonitrile reacts at 150° to form 2′ : 4′-*dinitrostilbene*-2-*carboxylic acid*, $CO_2H\cdot C_6H_4\cdot CH\colon CH\cdot C_6H_3(NO_2)_2$, m. p. 176—177°, 2′-*nitro*-4′-*cyanostilbene*-2-*carboxylic acid*, m. p. 227°, and 4′-*nitro*-2′-*cyanostilbene*-2-*carboxylic acid*, m. p. 182°, respectively (compare Thiele and Escales, Abstr., 1901, i, 689; Ullmann and Gschwind, Abstr., 1908, i, 622). In the condensation, the elimination of carbon dioxide from the extra-nuclear carboxylic group of the phthalonic acid is proved by the fact that 2-nitro-4-cyanostilbene is obtained by heating *o*-nitro-*p*-toluonitrile and benzoylformic acid with a little piperidine at 120—140°.

The behaviour of the two preceding nitrocyanostilbenecarboxylic acids on esterification is interesting. When heated with methyl-alcoholic hydrogen chloride, 2′-nitro-4′-cyanostilbene-2-carboxylic acid yields *methyl* 2′-*nitrostilbene*-2 : 4′-*dicarboxylate*,

$$CO_2Me\cdot C_6H_4\cdot CH\colon CH\cdot C_6H_3(NO_2)\cdot CO_2Me,$$

m. p. 138°, which is hydrolysed by a mixture of sulphuric and acetic acids and water to the corresponding *acid*, $C_{16}H_{11}O_6N$, m. p. 257°. 4′-Nitro-2′-cyanostilbene-2-carboxylic acid, however, is converted by methyl-alcoholic hydrogen chloride only into *ethyl* 4′-*nitro*-2′-*cyano*-

stilbene-2-carboxylate, m. p. 133°; when the acid is kept in concentrated sulphuric acid for a day and the product is boiled with aqueous sodium carbonate, 4′-*nitrostilbene*-2 : 2′-*dicarboxylic acid*, m. p. 248°, is obtained. Similarly, 2-nitro-4-cyanostilbene (Ullmann and Gschwind, *loc. cit.*) is converted by methyl-alcoholic hydrogen chloride into *methyl* 2-*nitrostilbene*-4-*carboxylate*, m. p. 122° (the corresponding *ethyl* ester has m. p. 124—125°), whilst 4-nitro-2-cyanostilbene is unchanged under the same conditions. Also it is known that *o*-nitro-*p*-toluonitrile is hydrolysed by methyl-alcoholic hydrogen chloride, whilst *p*-nitro-*o*-toluonitrile is unchanged. From these examples it is tolerably certain that the hydrolysis of the cyano-group, when it does take place, is preceded by the formation of an imino-ether, since Pinner has shown that imino-ethers are not formed under normal conditions by nitriles which contain a methyl group in the ortho-position.

4-*Nitrostilbene*-2-*carboxylic acid*, $CHPh{:}CH{\cdot}C_6H_3(NO_2){\cdot}CO_2H$, m. p. 206°, is produced by heating benzaldehyde and methyl *p*-nitro-*o*-toluate with a little piperidine at 200°. C. S.

The Reduction of Unsaturated Compounds. Aladar Skita and Carl Paal (D.R.-P. 230724. Compare Abstr., 1905, i, 397, 533; 1907, ii, 559; 1908, i, 599).—Much work has previously been recorded on the reduction of unsaturated compounds with hydrogen in the presence of palladium and a colloid; the employment of gum arabic and palladous chloride is now described, and the following compounds were obtained.

Ethyl 1-*methyl*cyclo*hexan*-3-*one*-6-*carboxylate*, an oil, b. p. 127—129°/15 mm., by the reduction of *ethyl* 1-*methyl*cyclo*hexen*-3-*one*-6-*carboxylate*, b. p. 142°/15 mm. 2 : 2 : 6-*Trimethylhexahydrobenzaldehyde*, b. p. 58—60°/10 mm., from *cyclo*citral; and *dihydro*iso*phorol*, b. p. 172°, from phorone. F. M. G. M.

Basic Bismuth Salicylate. Max Nyman and Richard Björkstén (*Pharm. Zentr.-h.*, 1911, 52, 423—428).—Apart from the normal salt, $Bi(C_7H_5CO_3)_3,4H_2O$, prepared by Cousse (*Compt. rend.*, 1894, 119, 1220; compare Abstr., 1906, i, 665), two basic salts are supposed to exist, namely, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}BiO$ (*loc. cit.*) and $(OH{\cdot}C_6H_4{\cdot}CO{\cdot}O)_4Bi_2O$. The former is that recognised in most pharmacopeias, but it cannot be prepared, since in contact with water it is dissociated. The authors have tried the various methods described for the preparation of basic bismuth salicylate, and find that the process of Fischer and Grützner (Abstr., 1894, i, 416) gives the best results for pharmaceutical purposes. The salt thus prepared furnishes 0·641—0·648 gram of bismuth sesquioxide per gram of salt, and is free from nitric acid, alkalis, and extraneous organic matter.

T. A. H.

Preparation of Zinc Hydrogen Borodisalicylate. A. Foelsing (D.R.-P. 230725).—The preparation of borodisalicylic acid, with its lead and silver salts, has previously been recorded.

Zinc dihydrogen borodisalicylate was obtained by mixing the dry constituents according to the equation:

$$4HO\cdot C_6H_4\cdot CO_2H + 2H_3BO_3 + ZnCO_3 = Zn[O\cdot CO\cdot C_6H_4\cdot O\cdot B(OH)\cdot O\cdot C_6H_4\cdot CO_2H]_2 + 5H_2O + CO_2,$$

adding hot water and allowing the product to crystallise; it is a colourless, crystalline powder (m. p. 100—110°), with powerful astringent and antiseptic properties. F. M. G. M.

Preparation of Nitrothioxanthones and their Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 228756).—Mayer (Abstr., 1909, i, 823) stated that nitrodiphenyl-sulphide-carboxylic [nitrophenylthiolbenzoic] acids do not yield nitrothioxanthones when heated with sulphuric acid; it is now found that if sulphuric acid containing sulphur trioxide is employed, a satisfactory yield of the corresponding nitrothioxanthone is obtained. The preparation of 4-nitrothioxanthone (m. p. 216—218°) from 2-*o*-nitrophenylthiolbenzoic acid is described, whilst 2-*o*-nitro-*p*-sulphothiolsulphonyl- and 2-*p*-nitro-6-sulphophenyl-thiolbenzoic acids and 2-*p*-nitrophenylthiolbenzoic acid are stated to be also applicable for this reaction. F. M. G. M.

Isomerism and Desmotropism with Ethyl 2 : 6-Diphenyl*cyclo*hexen-4-one-1-carboxylate. WALTER DIECKMANN (*Ber.*, 1911, **44**, 975—981).—Ethyl 2 : 6-diphenyl*cyclo*hexen-4-one-1-carboxylate, as obtained by the elimination of water from the corresponding ethyl diphenyl*cyclo*hexanolonecarboxylate, gives no coloration with ferric chloride, is insoluble in aqueous alkali hydroxide and does not couple with diazobenzene; it is accordingly the ketonic form. Alkali ethoxide or hydroxide converts it into a yellow alkali salt, which when decomposed by mineral acids yields an ester which has the properties of an enol. This is relatively stable, but it is in time converted, particularly when warmed, into a second ketonic isomeride, which differs from the first in melting point and crystalline structure. Both ketonic forms are stable, but they pass over into one another when heated above 200° or when boiled in alcoholic solution with alkaline reagents, forming an equilibrated mixture in which the first-mentioned ketonic form predominates; this is, therefore, regarded as the more stable isomeride. The formulæ

$$CHPh<\begin{matrix}CH(CO_2Et)\cdot CPh\\CH_2\text{———}CO\end{matrix}>CH \quad (I.) \qquad CHPh<\begin{matrix}C(CO_2Et):CPh\\CH_2\text{———}CO\end{matrix}>CH_2 \quad (II.)$$

are ascribed to the two ketonic forms, (I) being the more stable and therefore assigned to the first-mentioned isomeride. Reasons are given for assigning the formula $CHPh<\begin{matrix}C(CO_2Et):CPh\\CH_2\text{——}C(OH)\end{matrix}>CH$ to the enolic form.

The *ketonic* ester (I) crystallises in colourless, prismatic needles, m. p. 114—115°, and forms a semicarbazone separating in slender, yellow needles, m. p. 183—186°.

The 3-*phenylhydrazone* of *ethyl* 2 : 6-*diphenyl*-Δ^1-cyclo*hexene*-3 : 4-*dione*-1-*carboxylate*, $CHPh<\begin{matrix}C(CO_2Et):CPh\\CH_2\text{———}CO\end{matrix}>C:N\cdot NHPh$, produced on

coupling the enolic ester with diazobenzene, separates in red needles, m. p. 135°.

The *ketonic* ester (II) crystallises in small, colourless, rhombic plates, m. p. 105—106°, and yields a semicarbazone, m. p. 218°. E. F. A.

1 : 5-Diketones. WALTER DIECKMANN and KARL VON FISCHER (*Ber.*, 1911, **44**, 966—974).—When phenyl styryl ketone is condensed with ethyl acetoacetate in presence of sodium ethoxide, in addition to the compound, m. p. 120°, described by Knoevenagel and Speyer (Abstr., 1902, i, 226), there is formed a second isomeride, m. p. 168—169°. Two isomerides are similarly formed by the condensation of ethyl benzoylacetate and styryl *iso*propyl ketone. One form only is obtained on condensing ethyl benzoylacetate with phenyl styryl ketone or benzylidenepinacolin. According to Rabe and Elze (Abstr., 1902, i, 709), the primary additive products are 1 : 5-diketones, and the isomerides of higher melting point are *cyclo*hexanolones. Isomerism is always observed when the formation of *cyclo*hexanolone is possible; neither isomeride gives a coloration with ferric chloride.

Whereas ethyl 2 : 4-diphenyl*cyclo*hexan-4-ol-6-one-1-carboxylate from phenyl styryl ketone and ethyl acetoacetate is readily converted in presence of sodium ethoxide or piperidine in alcoholic solution into ethyl 2 : 4-diphenyl-Δ^4-*cyclo*hexene-6-one-1-carboxylate, the isomeric ethyl 2 : 6-diphenyl*cyclo*hexan-2-ol-6-one-1-carboxylate does not undergo a similar transformation, and is completely stable when boiled with piperidine.

By the action of concentrated sulphuric acid, the corresponding *cyclo*hexenone derivatives are obtained so long as the elimination of water between the hydroxyl and hydrogen attached to a carbon next the ketocarbonyl group is possible. An exception is afforded by ethyl 2 : 6-diphenyl-3 : 3-dimethyl*cyclo*hexan-2-ol-6-one-4-carboxylate, which forms *cyclo*hexenone with great difficulty.

Alkali breaks down into their components all those 1 : 5-diketo-derivatives which are unable to form *cyclo*hexanolones, for example, ethyl $\alpha\gamma$-dibenzoyl-β-phenylbutyrate, etc. The breakdown is also rapid in the case of ethyl α-benzoyl-γ-*iso*butyryl-β-phenylbutyrate, but it does not take place with ethyl γ-benzoyl-α-acetyl-β-phenylbutyrate.

Ethyl γ-benzoyl-α-acetyl-β-phenylbutyrate, obtained by the condensation of the components in presence of traces of sodium ethoxide (compare Knoevenagel and Speyer, *loc. cit.*), has m. p. 120—121°; when more sodium ethoxide is used or the compound is set aside in alcoholic solution with piperidine, *ethyl* 2 : 4-*diphenyl*cyclo*hexan*-4-*ol*-6-*one*-1-*carboxylate*, $CH_2<\substack{CO\cdot CH(CO_2Et)\\ C(OH)Ph\cdot CH_2}>CHPh$, is obtained, crystallising in colourless needles, m. p. 168—169°. The corresponding *pyrazolone*, $C_{19}H_{18}O_2N_2$, obtained by interaction of the ester with excess of hydrazine hydrate, forms colourless prisms, m. p. 274—275°.

Ethyl α-benzoyl-γ-acetyl-β-phenylbutyrate,

$$CH_3\cdot CO\cdot CH_2\cdot CHPh\cdot CHBz\cdot CO_2Et,$$

is the primary additive product from the components in presence of traces of sodium ethoxide or piperidine. It separates in colourless needles, m. p. 100—101°.

Ethyl 2 : 6-*diphenyl*cyclo*hexan*-2-*ol*-4-*one*-1-*carboxylate*,

$$CH_2{<}\begin{matrix}CO\text{————————}CH_2\\C(OH)Ph{\cdot}CH(CO_2Et)\end{matrix}{>}CHPh,$$

prepared from the foregoing, forms colourless needles, m. p. 216—217°. When warmed with hydrazine in alcoholic acetic acid solution the corresponding *azine*, m. p. 248—250°, is obtained.

Ethyl α-*benzoyl*-γ-iso*butyryl*-β-*phenylbutyrate*,

$$COPr^{\beta}{\cdot}CH_2{\cdot}CHPh{\cdot}CHBz{\cdot}CO_2Et,$$

crystallises in slender, colourless needles, m. p. 98—99°. By the further action of sodium ethoxide or on boiling with piperidine, it is with difficulty in part converted into *ethyl* 2 : 6-*diphenyl*-3 : 3-*dimethyl*cyclo*hexan*-2-*ol*-4-*one*-1-*carboxylate*, which separates in slender needles, m. p. 160°.

Ethyl αγ-*dibenzoyl*-β-*phenylbutyrate* crystallises in colourless, slender needles, m. p. 138—140°. With hydrazine it yields a badly characterised *pyrazolone*, m. p. about 110°.

Ethyl α-*benzoyl*-γ-tert.-*butyryl*-β-*phenylbutyrate*,

$$CMe_3{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CHBz{\cdot}CO_2Et,$$

separates in colourless prisms, m. p. 141°.

ααγγ-Tetrabenzoyl-β-phenylpropane, $CHBz_2{\cdot}CHPh{\cdot}CHBz_2$, was obtained from a molecular mixture of phenyl styryl ketone and ethyl benzoylacetate in alcoholic solution at 38° in presence of traces of piperidine or sodium ethoxide. It forms colourless, slender needles, m. p. 154—155°, and is hydrolysed by sodium ethoxide to dibenzoylmethane. E. F. A.

Introduction of Several Phthaloyl Groups into Aromatic Hydrocarbons. I. Experiments with Diphenyl. ROLAND SCHOLL and WERNER NEOVIUS (*Ber.*, 1911, **44**, 1075—1090).—The importance recently acquired by dianthraquinonyl derivatives in the production of vat dyes has induced the authors to investigate methods of introducing several phthaloyl groups into aromatic hydrocarbons. Commencing with diphenyl, the authors show that the reaction between this hydrocarbon, phthalic anhydride, and aluminium chloride in the presence of carbon disulphide leads only to the formation of diphenyl-4-phthaloylic acid. When heated, best with zinc chloride at 280—285° for thirty minutes, this acid is converted into 2-*phenylanthraquinone*, $C_6H_3Ph{<}^{CO}_{CO}{>}C_6H_4$, yellow needles, m. p. 160—161°, which is isolated by reducing it with alkaline sodium hyposulphite at 70°, filtering, and oxidising the filtrate by a current of air. 2-Phenylanthraquinone has also been obtained by reducing diphenyl-4-phthaloylic acid, best by 2*N*-sodium hydroxide, zinc dust, and ammoniacal copper sulphate, to 4-phenyldiphenylmethane-2′-carboxylic acid, converting this by zinc chloride at 180—185° into 2-*phenyl*-9-*anthrone*, $C_6H_3Ph{<}^{CH_2}_{CO}{>}C_6H_4$, m. p. 144—145°, and oxidising the latter, best by Goldmann's method with bromine and glacial acetic acid. A boiling solution of 2-phenyl-9-anthrone in glacial acetic acid is oxidised by aqueous ferric chloride, yielding 2 : 2′-*diphenyl*-10 : 10′-*dianthrone*-9 : 9′,

$CO\left\langle\begin{matrix}C_6H_4\\C_6H_3Ph\end{matrix}\right\rangle CH\cdot CH\left\langle\begin{matrix}C_6H_4\\C_6H_3Ph\end{matrix}\right\rangle CO$, m. p. 222—222·5°, which forms a reddish-yellow solution in alcoholic potassium hydroxide.

Pawlewski's bis-diphenylyl-*o*-phthalide (in a purer state, m. p. 235—247°; the substance, however, is probably still a mixture) is obtained by heating diphenyl, phthalic anhydride, and aluminium chloride in nitrobenzene at 100° or, better, in fused phthalic anhydride at 130°.

The authors attained their object by heating an intimate mixture of diphenyl, phthalic anhydride, and aluminium chloride at 100° for nine and a-half hours. In addition to a little diphenyl-4-phthaloylic acid, the product contains 2-phenylanthraquinone, *diphenyl*-4:4′-*diphthaloylic acid*, $C_{12}H_8(CO\cdot C_6H_4\cdot CO_2H)_2$, and 4-(2″)-*anthraquinonylbenzophenone-2′-carboxylic acid*, $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_3\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CO_2H$, m. p. 217—230°. The separation of these three substances is difficult, but for the authors' purpose is unnecessary, since by heating the crude product with concentrated sulphuric acid at 100°, 2 : 2′-*dianthraquinonyl*, $C_{12}H_6\left(\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4\right)_2$, brownish-yellow needles, m. p. 387—388°, is easily isolated in the pure state.

[With KARL HOLDERMANN.]—2 : 2′-Dianthraquinonyl is also obtained by heating 2-iodoanthraquinone with copper powder at 230—240°, and finally at 300° in a current of carbon dioxide. It is converted by boiling nitric acid, D 1·45, into *dinitro*-2 : 2′-*dianthraquinonyl*, $C_{28}H_{12}O_8N_2$, m. p. about 330°; this is reduced by boiling aqueous sodium sulphide to *diamino*-2 : 2′-*dianthraquinonyl*, a reddish-brown powder, m. p. above 400°, which is reduced by alkaline sodium hyposulphite to a reddish-brown vat, which, unlike that from diamino-1 : 1′-dianthraquinonyl, dyes unmordanted cotton. C. S.

Introduction of Several Phthaloyl Groups into Aromatic Compounds. II. Derivatives of Diphenyl. ROLAND SCHOLL and CHRISTIAN SEER (*Ber.*, 1911, **44**, 1091—1103).—The behaviour of the methyl-, hydroxy-, and methoxy-derivatives of diphenyl has been examined under the same conditions as that of diphenyl itself (preceding abstract). When heated with aluminium chloride and phthalic anhydride in the presence of a solvent, di-*o*-tolyl (in carbon disulphide) yields 2 : 2′-*dimethyldiphenyl*-5 : 5′-*diphthaloylic acid*, $C_{12}H_6Me_2(CO\cdot C_6H_4\cdot CO_2H)_2$, m. p. 95—100°, di-*p*-tolyl (in carbon disulphide) yields 4 : 4′-*dimethyldiphenyl*-3-*phthaloylic acid*,

$$C_{12}H_7Me_2\cdot CO\cdot C_6H_4\cdot CO_2H,$$

m. p. 177—179°, and *pp*′-dimethoxydiphenyl (in nitrobenzene at 70—85°) yields 4 : 4′-*dihydroxydiphenyl*-3-*phthaloylic acid*,

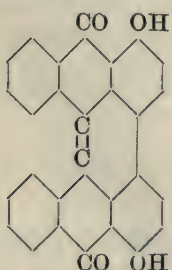
$$C_{12}H_7(OH)_2\cdot CO\cdot C_6H_4\cdot CO_2H,$$

m. p. 75—80°, whilst *pp*′-dihydroxydiphenyl is unattacked. The position of the phthaloyl groups in the preceding compounds is determined by the fact that di-*o*-tolyl forms a diphthaloylic acid, whilst diphenyl gives only a phthaloylic acid; consequently it is

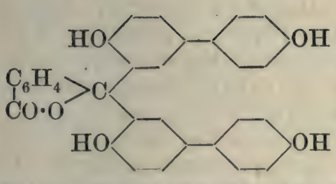
assumed that the methyl groups exert a greater orientating influence that the aryl group, and therefore the phthaloyl groups occupy para-positions to the methyl groups in the dimethyldiphenyldiphthaloylic acid, whilst in the dimethyldiphenylphthaloylic acid the phthaloyl group is in the ortho-position to the methyl group.

After the discovery that two phthaloyl groups can be introduced into diphenyl by heating it with aluminium chloride and phthalic anhydride (*loc. cit.*), *pp'*-dihydroxydiphenyl was heated under similar conditions. At 130—135° is produced a mixture of 4:4'-dihydroxydiphenyl-3-phthaloylic acid and 4:4'-*dihydroxy*-2:3-*phthaloyldiphenyl*-3'-*phthaloylic acid*, $C_6H_4{<}{\substack{CO \\ CO}}{>}C_6H_2(OH)\cdot C_6H_3(OH)\cdot CO\cdot C_6H_4\cdot CO_2H$, a reddish-brown, crystalline powder, m. p. 237—240°; the mixture is separated by taking advantage of the solubility of the *calcium* salt of the former acid in aqueous ammonia. 4:4'-*Dihydroxy*-1:1'-*dianthraquinonyl*, $C_{12}H_4(OH)_2\left({<}{\substack{CO \\ CO}}{>}C_6H_4\right)_2$, brown crystals, darkening at 325° and subliming at 360°, is produced when *pp'*-dihydroxydiphenyl or *pp'*-dimethoxydiphenyl is heated with aluminium chloride and phthalic anhydride at 150°. Under similar conditions at 160°, diresorcinol yields chiefly 2:4:2':4'-*tetrahydroxy*-1:1'-*dianthraquinonyl*, $C_{12}H_2(OH)_4\left({<}{\substack{CO \\ CO}}{>}C_6H_4\right)_2$, green needles, which does not melt at 320°, forms a sparingly soluble, violet *sodium* salt, and is reduced by alkaline hyposulphite, yielding a green and, finally, a reddish-brown vat, in which cotton is dyed red, the colour changing to brown in air, violet in alkalis, and green in acids.

Attempts to convert the preceding phthaloylic acids into derivatives of anthraquinone by the action of concentrated sulphuric acid have been only partly successful, the products containing considerable quantities of sulphonated substances. When zinc chloride is used instead of sulphuric acid, phthalide derivatives are produced; thus 4:4'-dimethyldiphenyl-3-phthaloylic acid and zinc chloride at 140—150° yield *di*-p-*tolylenephthalide*, $\begin{array}{l} C_6H_3Me \\ | \\ C_6H_3Me \end{array}{>}C{<}\begin{array}{l} -C_6H_4 \\ \quad | \\ O\cdot CO \end{array}$, colourless needles, m. p. 225—226°. 4:4'-*Dihydroxy*-meso-*benzdianthrone* (annexed formula), reddish-brown, metallic crystals, is obtained by treating a solution of 4:4'-dihydroxy-1:1'-dianthraquinonyl in concentrated sulphuric acid at 55—60° with copper powder. It forms a *dibenzoate*, m. p. 185—195° (decomp.), gives a solution in concentrated, sulphuric acid which is violet by reflected and cherry-red by transmitted light, and is reduced by alkaline hyposulphite to a green vat dye which is deposited on the fibre more easily in the cold than at higher temperatures, giving a colour of a brilliant orange-red tone after exposure to the air and treatment with sodium hypochlorite.



When zinc chloride is added to a mixture of *pp'*-dihydroxydiphenyl



and phthalic anhydride at 185° and the temperature is then kept at 205° for seven hours, a *phthalide* which probably has the annexed constitution is formed. It sinters above 260°, has m. p. 300—310°, and gives only a faintly reddish-brown solution in hot dilute sodium hydroxide, since the hydroxy-groups are not in the para-positions to the triphenylmethane carbon atom. C. S.

Transformation of Allylphthalimide into Propenylphthalimide. TREAT B. JOHNSON and D. BREESE JONES (*Amer. Chem. J.*, 1911, **45**, 343—356).—By the action of ethyl sodiomalonate on γ-bromopropylphthalimide, Gabriel (Abstr., 1890, 1129) obtained ethyl γ-phthalimidopropylmalonate. It was, therefore, expected that β-bromopropylphthalimide would react with ethyl sodiomalonate with formation of the isomeric ethyl β-methyl-γ-phthalimidoethylmalonate, $C_6H_4{:}(CO)_2{:}N{\cdot}CH_2{\cdot}CHMe{\cdot}CH(CO_2Et)_2$. It has been found, however, that when β-bromopropylphthalimide, prepared by the action of hydrogen bromide on allyl phthalimide (Seitz, Abstr., 1891, 1473), is heated with ethyl sodiomalonate, propenylphthalimide is obtained, together with ethyl malonate and a small quantity of a colourless, crystalline substance, m. p. 150—151°, isomeric with propenylphthalimide.

Propenylphthalimide, $C_6H_4{:}(CO)_2{:}N{\cdot}CH{:}CHMe$, m. p. 151°, forms stout, yellow crystals; it can also be obtained by the action of sodium phenoxide on β-bromopropylphthalimide. When heated with sodium ethoxide, it is converted into *propenylphthalamic acid*,

$$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CH{:}CHMe,$$

m. p. 152°, which is obtained as a viscous liquid and slowly changes to a crystalline solid. As allylphthalamic acid does not show this behaviour, it is suggested that propenylphthalamic acid exists in *cis*- and *trans*-modifications, one liquid at the ordinary temperature and the other solid. Propenylphthalamic acid can also be obtained by the action of sodium ethoxide on β-bromopropylphthalimide.

Allylphthalamic acid, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH{:}CH_2$, m. p. 112°, obtained by the action of sodium ethoxide or alcoholic potassium hydroxide on allylphthalimide, crystallises readily, and, on prolonged heating with alkali hydroxide, is decomposed with formation of allylamine and *o*-phthalic acid.

Lists are given of organic radicles which favour the production of propenyl compounds and allyl compounds respectively. E. G.

Preparation of *o*-Nitroanthraquinonecarboxylic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 229394).—*o*-Nitroanthraquinonecarboxylic acids containing the nitro- and carboxylic groups in adjacent positions have not previously been prepared, as the nitro-group invariably entered the unsubstituted ring.

1-*Nitroanthraquinone-2-carboxylic acid*, faintly-coloured needles, m. p. 285—287°, is prepared by the oxidation of 1-nitro-2-methylanthraquinone with chromic acid, or in nitric acid (40° Bé) solution.

F. M. G. M.

[Preparation of Diaminocarboxydiphenyl Ethers.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 229966).—When diazotised aminophenols and aminocresols containing substituted nitro-groups or halogens (but not SO_3H or CO_2H) are coupled with substituted diphenyl ethers, valuable colouring matters are obtained.

The *diaminocarboxydiphenyl ethers* are prepared by the condensation of 4-chloro-1 : 3-dinitrobenzene with hydroxybenzoic acids in the presence of acid absorbing reagents and subsequent reduction; they possess both acidic and basic functions, are crystalline, sparingly soluble in water, and yield salts with either bases or acids (not acetic acid).

2 : 4-*Diamino-4′-carboxydiphenyl ether*, m. p. 190°, and 2 : 4-*diamino-3′-carboxydiphenyl ether*, m. p. 225°, when coupled with diazotised 6-chloro-4-nitro-2-aminophenol and picramic acid respectively, yielded azo-*dyes*, the properties of which are described in the patent.

F. M. G. M.

Preparation of *o*-Carboxylic Derivatives of Arylthiolacetic Acids. RUDOLF LESSER (D.R.-P. 229067).—The *o*-carboxylic derivatives of arylthiolacetic acids of the typical formula

$$CO_2H\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2H$$

can be technically prepared by treatment in aqueous solution (or fusion without solvent) of esters of the type $CO_2H\cdot C_6H_4\cdot S\cdot CS\cdot OEt$ with chloroacetic acid; a 93% yield of *o*-carboxyphenylthiolacetic acid is thus obtained from diazotised anthranilic acid by treating it with a hot aqueous solution of potassium xanthate, and acting on the product with chloroacetic acid.

5-*Acetylamino-2-carboxyphenylthiolacetic acid* is prepared from 4-acetylaminoanthranilic acid (m. p. 193—194°); it crystallises from hot water and sinters about 249°.

2-*Carboxy-5-methoxyphenylthiolacetic acid*, m. p. 224—225°, is obtained from 4-methoxyanthranilic acid.

2-*Amino-4-ethylthiolbenzoic acid*, m. p. 168°, is prepared by treating diazotised *o*-nitro-*p*-aminobenzoic acid with potassium xanthate, followed by ethylation and subsequent reduction; the amino-compound when diazotised and treated with hot potassium xanthate and chloroacetic acid yields 2-*carboxy-5-ethylthiolphenylthiolacetic acid*, which forms yellowish-white crystals, m. p. 188°.

5-*Ethoxyanthranilic acid*, m. p. 174° (decomp.), obtained from *p*-aminophenol-*m*-carboxylic acid, furnishes subsequently 2-*carboxy-4-ethoxyphenylthiolacetic acid*, which forms yellow needles, m. p. 186—187°.

5-*Chloro-2-carboxyphenylthiolacetic acid*, m. p. 190—195°, is prepared by heating *ethyl -chloro-2-carboxyphenylxanthate* with chloroacetic acid at 150—170°. F. M. G. M.

Acylation of Oxalylbenzylcyanide [Oxalylphenylacetonitrile] and Oxalylethylenecyanide [Oxalylsuccinonitrile]. WALTER DIECKMANN (*Ber.*, 1911, 44, 981—990).—Oxalylphenylacetonitrile reacts with phenyl carbimide to form the *anil* of O-*carboxy-β-cyano-α-hydroxy-β-phenylpropenoic acid.* This compound is broken down by

sodium ethoxide in alcoholic solution into oxalylphenylacetonitrile and phenylurethane, whereas methyl-alcoholic potassium hydroxide produces an intense red compound, which is regarded as *iminohydroxymaleinanil*, $NPh<\begin{matrix}C(:NH)\cdot CPh \\ CO\text{———}C\cdot OH\end{matrix}$.

Similarly, oxalylsuccinonitrile and phenylcarbimide interact to form the *anil* of O-*carboxy-βδ-dicyano-α-hydroxy-Δ^α-pentenoic acid.*

On the other hand, according to Wislicenus (Abstr., 1908, i, 965), oxalylsuccinonitrile and phenyl carbamide interact to form a normal *O*-carbanilide. It is now shown that this is not hydrolysed by alcoholic sodium ethoxide, forms salts, and is converted by alkali into the corresponding carboxylic acid.

Whereas oxalylphenylacetonitrile and oxalylglutaronitrile form normal *O*-acyl derivatives, *β*-oxalylsuccinonitrile under similar conditions forms acyl derivatives, which are not hydrolysed by sodium ethoxide, form salts, and are converted by alkaline hydroxide into the corresponding carboxylic acids. They cannot accordingly be *O*-acyl derivatives, and are regarded as acyl derivatives of the isomeric *ethyl 5-amino-3-cyanofurfuran-2-carboxylate* of the constitution $\begin{matrix}CH\text{===}C(NHAc) \\ C(CN):C(CO_2Et)\end{matrix}>O$.

The same formula may be applied to *β*-oxalylsuccinonitrile, and is supported by the fact that it fluoresces in alcoholic solution and lacks the characteristic ketone reactions.

The *anil* of O-*carboxy-β-cyano-α-hydroxy-β-phenylpropenoic acid*,

$$NC\cdot CPh:C<\begin{matrix}CO\cdot NPh \\ O\text{—}CO\end{matrix},$$

forms colourless, slender needles, m. p. 210°.

The *anil* of O-*carboxy-βδ-dicyano-α-hydroxy-Δ^α-pentenoic acid*,

$$NC\cdot CH_2\cdot CH_2\cdot C(CN):C<\begin{matrix}CO\cdot NPh \\ O\text{—}CO\end{matrix},$$

crystallises in colourless prisms, m. p. 133°. Neither of these compounds could be converted into an isomeride.

The *N*-carbanilide of ethyl 5-amino-3-cyanofuran-2-carboxylate, $O<\begin{matrix}C(NH\cdot CO\cdot NHPh):CH \\ C(CO_2Et)\text{=====}C\cdot CN\end{matrix}$, prepared by the interaction of phenylcarbimide and *β*-oxalylsuccinonitrile, is identical with the compound described by Wislicenus (*loc. cit.*). The corresponding *acid* forms microscopic crystals, m. p. 210° (decomp.); the *acetyl* derivative, $O<\begin{matrix}C(NHAc):CH \\ C(CO_2Et)=C\cdot CN\end{matrix}$, prepared by heating *β*-oxalylsuccinonitrile with acetic anhydride, crystallises in colourless needles, m. p. 177°. Sodium methoxide converts it into the corresponding *methyl* ester, colourless, prismatic needles, m. p. 197°. The colourless alcoholic solution of the ester shows a faint yellow coloration, and an intense blue fluorescence on the addition of alcoholic potassium hydroxide. On hydrolysis, the acetyl ester is converted into 5-*acetylamino-3-cyanofuran-2-carboxylic acid*, $O<\begin{matrix}C(NHAc):CH \\ C(CO_2H)=C\cdot CN\end{matrix}$, which crystallises in colourless prisms, m. p. 249° (decomp.).

Ethyl-5-benzoylamino-3-cyanofuran-2-carboxylate, prepared by the action of benzoyl chloride on β-oxalylsuccinonitrile in pyridine solution, crystallises in slender, colourless needles, m. p. 168—169°. The corresponding *acid* is obtained in colourless, microscopic prisms, m. p. 256° (decomp.). It forms a sparingly soluble *acid sodium* salt, crystallising in colourless needles. E. F. A.

α-Phenyltricarballylic Acid. RUDOLF WEGSCHEIDER (*Ber.*, 1911, **44**, 908—909).—The α-phenyltricarballylic acid described by Hecht (Abstr., 1903, i, 700) melts at 110—115°, then solidifies, and finally melts again at 196—201°. It is probably identical with the α-phenyltricarballylic acid, having m. p. 199°, obtained by Stobbe and Fischer (Abstr., 1901, i, 276), the difference in the melting points being due to water of crystallisation. F. B.

Synthesis of Spyrocyclic Compounds. DAN RADULESCU (*Ber.*, 1911, **44**, 1018—1022. Compare Abstr., 1909, i, 652).—By the condensation of ethyl succinate and ethyl *cyclo*propane-1 : 1-dicarboxylate in ether in presence of sodamide there is formed an *ester acid* and the corresponding *dibasic acid*.

The former, *ethyl hydrogen* cyclo*propane*cyclo*pentane*-(1 : 1)-*spiran*-2 : 5-*dione*-3 : 4 *dicarboxylate*, $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CO\cdot CH\cdot CO_2Et \\ | \\ CO\cdot CH\cdot CO_2H \end{matrix}$, crystallises in slender, transparent, lustrous plates, m. p. 153—154° (decomp.), with liberation of carbon dioxide; it turns blue at 180—190° (decomp. again at 250°). When crystallised repeatedly from boiling water, it loses alcohol and forms the dibasic acid, which is converted into the ester by partial esterification. Both acids give the intense violet coloration characteristic of β-ketonic acids with ferric chloride. They are decomposed almost quantitatively by alkali hydroxides into succinic acid and *cyclo*propane-1 : 1-dicarboxylic acid.

cyclo*Propane*cyclo*pentane*-(1 : 1)-*spiran*-2 : 5-*dione*-3 : 4-*dicarboxylic acid*, $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CO\cdot CH\cdot CO_2H \\ | \\ CO\cdot CH\cdot CO_2H \end{matrix}$, crystallises with H_2O in leaf-like needles, m. p. 161° (decomp.). At higher temperatures a mixture of the blue compound and a granular anhydride are formed. E. F. A.

[Preparation of Triphenylmethane Derivatives.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 228838).—Numerous condensation products of the hydroxybenzaldehydes have been described previously; the work has now been extended to the compounds obtained by the condensation of *o*- and *p*-hydroxybenzaldehydes with aromatic carboxylic acids, and the subsequent oxidation of the leuco-compounds.

p-Hydroxybenzaldehyde (14 parts), *o*-cresotic acid (33 parts), 300 parts of sulphuric acid (60° Bé), and acetic acid (50 parts) are stirred together at a temperature of 70° during twenty hours, poured on to ice, and the dried product subsequently oxidised by air, or by treatment with hydrogen nitrosyl sulphate in sulphuric acid solution; the *product*, a reddish-brown powder, is sparingly soluble in water, and readily

so with an intense red coloration in sodium hydroxide. The *p*-hydroxybenzaldehyde was also heated at 60—70° with sulphuric acid containing anhydride, and the sulphonated product subsequently condensed with *o*-cresotic acid, yielding an aqueous soluble *product*. The following aldehydes are described: 3-*chloro*-2-*hydroxybenzaldehyde*, m. p. 54°; 4-*hydroxy*-3-*tolualdehyde*-5-*sulphonic acid* yields an orange crystalline *product* with *p*-toluidine in acetic acid solution, and with phenylhydrazine in the same solvent a colourless, crystalline precipitate; 4-*hydroxybenzaldehyde*-3-*sulphonic acid* yields a similar precipitate with phenylhydrazine; 4-*hydroxybenzaldehyde*-2-*sulphonic acid* yields a red precipitate with benzidine. A tabulated list of condensation products from these and other derivatives of hydroxybenzaldehyde with *o*-cresotic acid, and the colours of their solutions in various solvents is also appended. F. M. G. M.

Trimethylene [*cyclo*Propane] Derivatives. LOUIS MICHIELS (*Bull. Soc. chim. Belg.*, 1911, **25**, 177—178).—The formula $C_3H_5 \cdot CO \cdot CH_2Cl$ already assigned to *cyclo*propyl chloromethyl ketone (this vol., i, 63) is confirmed by the fact that the corresponding nitrile gives a violet coloration with ferric chloride.

*cyclo*Propylethylpropylcarbinyl bromide (*loc. cit.*) when left in contact with hydrobromic acid furnishes a *dibromide*, D^{20} 1·3848, indicating that the elements of hydrogen bromide are as easily added to the *cyclo*propane nucleus of tertiary alcohols as to that of the primary or secondary alcohols (*loc. cit.*). T. A. H.

New Mordant Dyes derived from Gallic Acid. ED. EHRMANN (*7th Inter. Congr. Appl. Chem.*, 1909, Sect. IVB, 76—77).—A blue dye is obtained on heating in a sealed tube at 150° for five hours a mixture of gallic acid, diphenyl-*m*-phenylenediamine, and phosphoryl chloride. The substance gives a brown coloration with concentrated sulphuric acid, and is soluble in alkali hydroxides. To it is assigned the structure of 3:4:5-*trihydroxy*-2:4-*diphenyldiaminobenzophenone*, $C_6H_2(OH)_3 \cdot CO \cdot C_6H_3(NHPh)_2$.

When a mixture of gallic acid, *m*-hydroxydiphenylamine, and phosphoryl chloride is heated in a sealed tube for four hours at 155°, a red dye is produced, which is probably a *tetrahydroxyanilinobenzophenone*, $C_6H_2(OH)_3 \cdot CO \cdot C_6H_3(NHPh) \cdot OH$. This substance is also soluble in alkalis.

Both dyes dye cotton previously treated with metallic mordants; the blue dye gives with iron a greyish-blue, with chromium a violet-blue, and with aluminium a clear blue. The red substance yields with iron a brownish-red, and with aluminium a yellowish-red. R. V. S.

Ketens. III. Action of Diphenylketen on Quinones. HERMANN STAUDINGER and ST. BEREZA (*Annalen*, 1911, **380**, 243—277).—Diphenylketen reacts with quinones in much the same manner as with unsaturated ketones (compare Abstr., 1908, i, 410; 1910, i, 46). Almost any quinone in which the two ortho-positions with respect to one carbonyl group are unsubstituted reacts in the cold with a molecular proportion of diphenylketen, yielding *β*-lactones of

the type $O:C_6H_4<\substack{CPh_2\\ O}>CO$. Benzoquinone, toluquinone, chlorobenzoquinone, and *m*-dichlorobenzoquinone react in this manner. When there are substituents in the positions ortho to both carbonyl groups, for example, xyloquinone, *p*-dichlorobenzoquinone, and trichloroquinone, the reaction proceeds very slowly, and when all four ortho-positions are substituted, as in chloranil, the reaction is completely inhibited. These results may be due to "steric hindrance," to a diminution in the basic character of the oxygen atom of the carbonyl group, or to a diminution of isorropesis; but the authors suggest the following explanation. Previous experiments have shown that the unsaturated character of the carbonyl group is increased by the presence of an olefine linking (Abstr., 1910, i, 46), and it is known that a chlorine substituent diminishes the unsaturated nature of an olefine compound. The ethylene linkings in chloranil are thus less reactive than those in benzoquinone, and therefore have a much smaller effect in increasing the unsaturated character of the carbonyl groups; in other words, the carbonyl groups in chloranil are somewhat more saturated than those in quinone. Kehrmann's observations on quinhydrone formation are in harmony with this view. Naphthaquinone yields a β-lactone less readily than benzoquinone does, and anthraquinone does not react in the cold with diphenylketen.

When an excess of diphenylketen is used in the cold, both carbonyl groups of a quinone can react, provided neither group is ortho-substituted. In such cases, and even in the case of toluquinone, unstable dilactones are formed, which are immediately transformed into the corresponding quinodimethanes by the elimination of 2 molecules of carbon dioxide:

$$CO<\substack{CPh_2\\ O}>C_6H_4<\substack{CPh_2\\ O}>CO \longrightarrow CPh_2:C_6H_4:CPh_2 + 2CO_2$$

(compare Abstr., 1904, i, 491; 1908, i, 411).

The β-lactones are quinol derivatives, and are colourless; they give the usual carbonyl reactions, for example, yield phenylhydrazones, but these, unlike most of the phenylhydrazones of quinols (Bamberger, Abstr., 1902, i, 509), yield azo- and not benzene derivatives. When the solid β-lactone from quinone is exposed to sunlight, or when its benzene solution is boiled in bright sunlight, molecular rearrangement occurs, and the γ-lactone of 2:5-dihydroxytriphenylacetic acid, $OH\cdot C_6H_3<\substack{O\\ CPh_2}>CO$, is formed by the wandering of an alkyl group (compare Bamberger, Abstr., 1901, i, 141; 1907, i, 516). This rearrangement occurs in the absence of water, and is not therefore due to addition and subsequent removal of water. With a methyl-alcoholic solution of sulphuric acid (compare Bamberger) an additive compound of the β-lactone and methyl alcohol is obtained. When heated carefully below their melting points, the β-lactones yield carbon dioxide and the normal product, namely, a quinomethane; but when decomposed by heating until they melt, or by heating with a solvent of high boiling point, the products are carbon dioxide and a quinodimethane, provided the lactone is derived from a quinone with two reactive

carbonyl groups. The formation of a quinodimethane under these conditions is probably due to the conversion of the β-lactone into diphenylketen and the quinone, the subsequent formation of a β-dilactone, and the decomposition of this into carbon dioxide and a quinodimethane.

The following numbers give the percentage of the quinone which has reacted when heated with two gram-molecules of diphenylketen at 130° for 1·5 hours: benzoquinone 70, toluquinone 71·5, xyloquinone 50, chlorobenzoquinone 27, *p*-dichlorobenzoquinone 17, *m*-dichlorobenzoquinone 14, trichlorobenzoquinone 6, tetrachlorobenzoquinone 3, naphthaquinone 72, and anthraquinone 2. The amount of decomposition of the β-lactones has been studied by measuring the volume of carbon dioxide formed when the lactones decompose, and also the addition of keten to the quinomethane (1 mol.) by measuring the carbon dioxide evolved. In the latter case the reaction proceeds violently, and gives a 95% yield of carbon dioxide in the case of the quinomethane derived from *m*-dichlorobenzoquinone, and only a 74% yield in the case of diphenylquinomethane.

The β-*lactone* of toluquinoldiphenylacetic acid,

$$O{:}C_6H_3Me{<}\genfrac{}{}{0pt}{}{CPh_2}{-O-}{>}CO,$$

crystallises from ether, and has m. p. 123° (decomp.); the β-*lactone* from xyloquinone, $C_{22}H_{18}O_3$, crystallises from ether in large, colourless plates, m. p. 123—124° (decomp.); the β-*lactone* from chlorobenzoquinone, $C_{20}H_{13}O_3Cl$, crystallises from acetone, and has m. p. 129—130° (decomp.); the β-*lactone* from *m*-dichlorobenzoquinone, $C_{20}H_{12}O_3Cl_2$, has m. p. 143° (decomp.), and the isomeric β-*lactone* from *p*-dichlorobenzoquinone crystallises from acetone in colourless needles, m. p. 180—192° (decomp.). The β-*lactone* from *m*-dibromobenzoquinone, $C_{20}H_{12}O_3Br_2$, has m. p. 141° (decomp.); the *lactone* from trichlorobenzoquinone, $C_{20}H_{11}O_3Cl_3$, is sparingly soluble, crystallises from dichloroethylene, and has no definite m. p. The β-*lactone* from α-naphthaquinone, $C_{24}H_{16}O_3$, has m. p. 127°.

Well-defined compounds could not be obtained by the hydrolysis of the β-lactone from benzoquinone. The *phenylhydrazone* of the lactone crystallises from dichloroethylene at 0°, and, after recrystallisation from glacial acetic acid, forms red crystals, $C_{26}H_{20}O_2N_2$, m. p. 180° (decomp.). When heated, it evolves carbon dioxide, and forms a tarry mass. The γ-*lactone* of 2 : 5-dihydroxytriphenylacetic acid, $C_{20}H_{14}O_3$, obtained by the action of sunlight on the β-lactone from benzoquinone, or prepared by the condensation of benzilic acid with quinol in the presence of benzene and stannic chloride, separates from methyl alcohol or glacial acetic acid in large, colourless crystals, m. p. 196°, and gives a pale brown coloration with warm concentrated sulphuric acid.

The isomeric γ-*lactone* of 2 : 4-dihydroxytriphenylacetic acid, obtained by condensing benzilic acid with resorcinol in the presence of benzene and stannic chloride, crystallises from benzene and has m. p. 167°. The corresponding *acid* has m. p. 140°, but is gradually transformed into the lactone.

The *additive* compound of the β-lactone and acetic acid,

$$OH\cdot C\ll\begin{matrix}CH\cdot CH(OAc)\\CH=\!=\!=CH\end{matrix}\!>\!C\!<\!\begin{matrix}CPh_2\\-O-\end{matrix}\!>\!CO(?),$$

forms colourless crystals from glacial acetic acid, and has m. p. 165°. With concentrated sulphuric acid, it gives the reddish-violet coloration of benzilic acid; it does not react with bromine, phenylhydrazine, or semicarbazide, and does not combine with methyl alcohol. When warmed with alkali in the absence of air, it yields benzilic acid and quinol. The *additive* compound of the β-lactone with methyl alcohol, $C_{21}H_{18}O_4$, forms large, colourless crystals, m. p. 122—123°, and with warm alkali yields methoxydiphenylacetic acid, $C_{15}H_{14}O_3$, m. p. 111—112°.

Diphenylquinomethane is best prepared by heating the β-lactone under reduced pressure for four days at 88°, then for two days at 110°, and crystallising from pure carbon disulphide. It may also be prepared by prolonged boiling of a benzene solution of the lactone in the dark, in an atmosphere of carbon dioxide to prevent oxidation. The compound obtained from the β-lactone from toluquinone is identical with the product, m. p. 176°, prepared by Bistrzycki and Zurbringen (Abstr., 1904, i, 44).

Diphenylchloroquinomethane, $O\!:\!C_6H_3Cl\!:\!CPh_2$, separates from carbon disulphide as red crystals, m. p. 157—160°, and the corresponding m-*dichloro*-derivative, $C_{19}H_{12}OCl_2$, forms red crystals, m. p. 215°. The *m*-dibromo-derivative is identical with Auwers' product (m. p. 231°) (compare Auwers and Schröter, Abstr., 1903, i, 820).

Tetraphenyltoluquinodimethane, $CPh_2\!:\!C_6H_3Me\!:\!CPh_2$, crystallises from acetone, and has m. p. 200—210°.

Tetraphenylchloroquinodimethane, $CPh_2\!:\!C_6H_3Cl\!:\!CPh_2$, also crystallises from acetone, and has m. p. 195—200°.

Tetraphenyl-m-*dichloroquinodimethane*, $CPh_2\!:\!C_6H_2Cl_2\!:\!CPh_2$, crystallises in glistening, deep red prisms, m. p. 225°.

The quinodimethanes may be prepared by a variety of methods, but in the majority of cases the best method is the fusion of diphenylketenquinoline with the necessary quinone in an atmosphere of carbon dioxide. J. J. S.

Ketens. IV. Phenylmethylketen. HERMANN STAUDINGER and LEOPOLD RUŽIČKA (*Annalen*, 1911, **380**, 278—303).—*Phenylmethylketen*, $CMePh\!:\!CO$, has been prepared in order to compare its properties with those of a purely aliphatic, and of a purely aromatic, keten. It is an orange-yellow liquid, paler in colour than diphenylketen, has b. p. 74°/12 mm. It combines with water to form α-phenylpropionic acid, and with aniline to form α-phenylpropionanilide. With benzylideneaniline it forms two distinct *products*, $C_{22}H_{19}ON$, by the union of 1 mol. of keten with one of the Schiff's base. They melt respectively at 125—126° and 146—147°. It also reacts with benzoquinone, and with quinoline forms a keten base, which is stable like that derived from dialkylketens. It polymerises only slowly, and is thus intermediate between dimethyl- and diphenyl-keten. The *polymeride*, $(C_9H_8O)_2$, has m. p. 161·5—162·5°, and is depolymerised when heated. A second polymeride, $(C_9H_8O)_n$, has m. p. 267° (decomp.). It has not

been found possible to obtain the keten from phenylmethylmalonic acid, as the latter does not yield an anhydride, but it can be prepared from phenylmethylchloroacetyl chloride and zinc.

Phenylmethylmalonyl chloride, $CMePh(COCl)_2$, obtained by the action of phosphorus pentachloride and pure ether on the corresponding acid, is a yellow oil, b. p. 114—115°/12 mm. A 60—65% yield of acetophenonecyanohydrin (Jacoby, Abstr., 1886, 800) can be obtained by using a solution of acetophenone in ether (1 : 4) and an excess of concentrated potassium cyanide solution and stirring automatically whilst concentrated hydrochloric acid is run in slowly. After hydrolysing the crude nitrile for two days with concentrated hydrochloric acid at the ordinary temperature, and removing the hydrogen chloride by a current of air, the mass is extracted several times with a mixture of light petroleum (2 parts) and ether (1 part) to remove acetophenone. The tetrahydro-oxazolone is precipitated, and the solution contains atrolactinic acid and its amide. *a-Phenyl-lactamide*, $C_9H_{11}O_2N$, crystallises from dichloroethylene in plates, m. p. 101—102°, and, when heated for an hour at 100° with 5% hydrochloric or sulphuric acid, yields the corresponding acid, but when boiled for a longer time appreciable amounts of *iso*atropic acid are formed (*Annalen*, 1879, **195**, 184).

Atropamide, $CH_2:CPh\cdot CO\cdot NH_2$, is sparingly soluble in water, and has m. p. 121—122°. 2:5-*Diphenyl*-2 : 5-*dimethyltetrahydro-oxazol*-4-*one*, $CMePh{<}{\overset{\text{—O—}}{\text{CO·NH}}}{>}CMePh$, crystallises from methyl alcohol in slender needles, m. p. 219—220°, and with phenylcarbimide it yields an additive *compound*, $C_{24}H_{22}O_3N_2$, m. p. 133—134°. It does not react with phenylhydrazine, and is hydrolysed when boiled for two hours with glacial acetic and concentrated hydrochloric acids to atropic acid and acetophenone. The oxazolone can be synthesised by keeping a mixture of a-phenyl-lactamide, acetophenone, and concentrated hydrochloric acid for three weeks.

a-Chloro-a-phenylpropionyl chloride is best obtained by carefully treating the hydrated atrolactic acid with phosphorus pentachloride (3 mols.), removing the oxy-chloride, and extracting with light petroleum. It is accompanied by $\alpha\beta$-dichloro-a-phenylpropionyl chloride, from which it can be freed by repeated distillation under very low pressures. It has b. p. 112—113°/12 mm., or 59—61°/0·02 mm. The *anilide*, $C_{15}H_{14}ONCl$, has m. p. 71—74°, and the p-*toluidide*, m. p. 91—92°. The *toluidide* of $\alpha\beta$-dichloro-a-phenylpropionic acid, $C_{16}H_{15}ONCl_2$, has m. p. 81—82·5°. The p-*toluidide* of *a-iso*atropic acid, $(C_{16}H_{15}ON)_2$, has m. p. 252°.

The crude chloride obtained from atrolactic acid when treated with *p*-toluidine yields the toluidides of a-chloro-a-phenylpropionic acid and of β-chloro-a-phenylpropionic acid. The latter *toluidide* is insoluble in light petroleum, crystallises from carbon disulphide, and has m. p. 182—182·5° (decomp.). β-Toluidine reacts with the product from atropic acid and phosphorus pentachloride, yielding the p-*toluidide* of atropic acid, $C_{16}H_{15}ON$, m. p. 229—231°, and the *p*-toluidide of $\alpha\beta$-dichloro-a-phenylpropionic acid.

a-Phenylpropionanilide, $C_{15}H_{15}ON$, crystallises from light petroleum, and has m. p. 133—134°. *Phenylmethylketenquinoline*, $C_{27}H_{23}O_2N$, crystallises from ethyl acetate in colourless needles, m. p. 175—175·5°, and when warmed with dilute hydrochloric acid yields an *acid*, $C_{27}H_{25}O_3N$, m. p. 94—96°. J. J. S.

Preparation of Acenaphthenone. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 230237).—*a-Naphthylacetyl chloride*, a yellow oil with penetrating odour, b. p. 188°/23 mm., is dissolved in nitrobenzene and slowly treated with aluminium chloride in the same solvent; the product is poured on ice, and the acenaphthenone formed in this way is separated from nitrobenzene by means of steam and distilled under reduced pressure. F. M. G. M.

Benzylidenediacetyl [Styryl Methyl Diketone]. OTTO DIELS and ERICH ANDERSONN (*Ber.*, 1911, **44**, 883—888).—Although styryl methyl diketone cannot be prepared by the direct condensation of diacetyl and benzaldehyde, several of its derivatives have been obtained by condensing benzaldehyde with the substituted hydrazones of diacetyl. Of these derivatives only the acetyl compound could be transformed into styryl methyl diketone.

Benzylidenediacetylphenylmethylhydrazone,

CHPh:CH·CO·CMe:N·NMePh,

prepared by condensing benzaldehyde with diacetylphenylmethylhydrazone by means of sodium hydroxide in methyl-alcoholic solution, crystallises in citron-yellow needles, m. p. 138—139°.

The corresponding *phenylhydrazone*, CHPh:CH·CO·CMe:N·NHPh, obtained in a similar manner, forms yellow needles, m. p. 189—190° (corr.).

Styryl methyl diketone monoacetylhydrazone,

CHPh:CH·CO·CMe:N·NHAc,

prepared by the condensation of diacetylmonoacetylhydrazone and benzaldehyde with aqueous barium hydroxide, crystallises in needles having a green lustre, m. p. 185—186°.

Styryl methyl diketone, CHPh:CH·CO·COMe, is obtained in a yield of 8% by distilling the monoacetylhydrazone with dilute sulphuric acid. It crystallises from light petroleum in yellow leaflets, m. p. 52—53°, and on treatment with phenylhydrazine yields the above-mentioned phenylhydrazone. When kept it is transformed into an almost colourless substance, which crystallises from alcohol in greenish needles, m. p. 168—169°. The constitution of the latter compound has not yet been determined. F. B.

Electrolytic Oxidation of *p*-Benzoquinone. RICHARD KEMPF (*J. pr. Chem.*, 1911, [ii], **83**, 329—394).—In order to examine systematically the course of the electrolytic oxidation of benzene it is necessary first to study the oxidation of *p*-benzoquinone, the chief product of the reaction. The apparatus is figured and described in detail. It consists essentially of the electrolytic vessel divided by a porous partition into cathodic and anodic compartments. The latter is as small as possible (200 c.c.) compared with the area of the anode, which consists of a lead disk, 2 mm. thick, 17 cms. in diameter,

making 100—120 revolutions per minute. The electrolytes in the cathodic and anodic compartments are 30% and 10% sulphuric acids respectively. At the top of the anodic compartment is connected an apparatus for collecting the gases evolved. The electrolytic vessel is completely immersed in a bath of flowing water. Nine experiments are described in which the amount of *p*-benzoquinone varies between 15 and 25 grams, the amount of 10% sulphuric acid between 200 and 250 c.c., the current between 4 and 5 amperes (at 3·4 volts), and the time between six and ten hours. The results are similar to those obtained by the oxidation of *p*-benzoquinone by silver peroxide (Abstr., 1907, i, 63). Maleic, formic, and racemic acids are obtained together with carbon monoxide and dioxide, occasionally also an *acid*, $C_4H_4O_5$, m. p. 141·5—145·5° (corr.) (*barium* salt, $C_4H_2O_5Ba,2H_2O$), which is probably maleglycidic acid, $O<\begin{matrix}CH\cdot CO_2H \\ | \\ CH\cdot CO_2H\end{matrix}$. Possible methods by which these substances are produced are discussed. The author inclines to the view that in all processes of electrolytic oxidation the actual oxidising agent is a metallic peroxide formed by the action of the nascent oxygen on the anode. C. S.

Structure of Naphthaquinone Derivatives. II. OSWALD MILLER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 440—454. Compare this vol., i, 308).—The m. p. (decomp.) of 1 : 2 : 4-hydroxynaphthaquinone varies, according to the source of the compound, from 183° to 191°. This variation is apparently not due to inaccuracy of reading the m. p owing to decomposition, and is also far greater than would be caused by differences in the size of the crystals.

Conversion of the hydroxynaphthaquinone, m. p. 191°, into the ethyl ether results in the formation of two ethers : (1) O : O : OEt = 1 : 2 : 4, m. p. 127°, and (2) O : O : OEt = 1 : 4 : 2, m. p. 98°. Hydroxynaphthaquinone must hence be regarded as an equilibrated mixture of the dynamic isomerides corresponding with these two ethers.

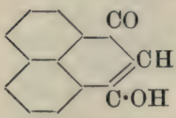
When this mixture is treated with aniline so as to form the anilide, virtually only the first of the two forms reacts, the velocity in the case of the latter being nearly zero. But, as the yield of anilide approximates to the theoretical, the formation of the anilide from form (1) is accompanied by transformation of the inactive compound into the active one. T. H. P.

***peri*-Naphthindandione.** GIORGIO ERRERA (*Gazzetta*, 1911, **41**, i, 190—197).—The aim of the work here described was to prepare from naphthalic acid a compound corresponding with indandione (diketohydrindene) and to ascertain whether ethyl acetoacetate and ethyl malonate act on naphthalic anhydride in the same manner as on phthalic anhydride (compare Gabriel, Abstr., 1884, ii, 176).

Ethyl naphthalate, $C_{10}H_6(CO_2Et)_2$, obtained together with ethyl sodioacetoacetate by heating a mixture of methyl naphthalate and excess of ethyl acetate with sodium, forms transparent crystals, m. p. 54·5°.

Naphthalic anhydride does not react with ethyl malonate in

presence of sodium acetate (Gabriel, *loc. cit.*), but when zinc chloride is used as condensing agent, the reaction yields *peri-naphthindandione* (annexed formula), which forms golden-yellow plates or needles, or reddish-brown crystals, m. p. 265° (decomp.), decomposition beginning at 250°. With methyl sulphate in potassium hydroxide solution, it gives the *methyl ether*, $C_{13}H_7O·OMe$, in hard, yellowish-brown plates, m. p. 144°. The *ethyl ether*, $C_{13}H_7O·OEt$, forms yellowish-brown crystals, m. p. 147·5° (compare Freund and Fleischer, Abstr., 1910, i, 490).



By treating *peri*-naphthindandione with phenylhydrazine, the following compounds were obtained: (1) a complex derivative of the naphthindandione, containing about 5% of nitrogen and forming golden-yellow scales, m. p. 260—265°; (2) pale brown, flattened needles, m. p. 128—129°, possibly acetylphenylhydrazine; (3) brown needles, m. p. 219°, probably consisting of the naphthindandionephenylhydrazone.

T. H. P.

Preparation of Halogenated Anthraquinones. Badische Anilin- & Soda-Fabrik (D.R.-P. 228876).—Halogenated anthraquinones can be readily prepared in aqueous solution by the action of sodium chlorate on the corresponding anthracenesulphonic acids. Sodium 1 : 8-anthracenedisulphonate (30 parts) is dissolved in water, hydrochloric acid added, and slowly treated with a solution of sodium chlorate (60 parts); the mixture is then heated at 100°, when 1 : 8-*dichloroanthraquinone*, m. p. 202—203°, separates in needles.

2-Chloroanthraquinone and 2 : 6- and 2 - 7-dichloroanthraquinones are similarly prepared.

F. M. G.M.

Preparation of Chloro-substitution Products of Anthraquinones and of Halogenated Anthraquinones. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 228901).—1 : 4 : 5 : 8-*Tetrachloroanthraquinone*, yellow needles, is obtained by heating anthraquinone (50 parts) dissolved in fuming sulphuric acid (500 parts) in the presence of iodine (1 part) to 130° and leading in chlorine until the required weight is absorbed. Two *hexachloroanthraquinones* are prepared in analogous manner from 2 : 6- and 2 : 7-dichloroanthraquinones, whilst β-chloroanthraquinone yielded a *pentachloroanthraquinone*.

F. M. G. M.

Anthraquinone Series. Fritz Ullmann (*Annalen*, 1911, **380**, 317—341).—I. [With Otto Fodor.]—*a-Aminoanthraquinone* (compare Abstr., 1910, i, 270, 751).—1-*p*-Toluenesulphonylaminoanthraquinone (*loc. cit.*, 751) has m. p. 228·5° (corr.). With concentrated sulphuric acid (10 parts) it yields an orange-coloured solution, which quickly turns yellow; after warming for a short time, the hydrolysis is complete, and on pouring on to ice-water pure 1-aminoanthraquinone (Abstr., 1897, i, 427) is obtained.

1-p-*Toluenesulphonylmethylaminoanthraquinone*,

$$C_6H_4{:}C_2O_2{:}C_6H_3·NMe·SO_2·C_6H_4Me,$$

obtained from 1-chloroanthraquinone and *p*-toluenesulphonylmethylamide, crystallises from alcohol in pale yellow plates, or large, glisten-

ing needles, m. p. 198° (corr.), and on hydrolysis with concentrated sulphuric acid yields 1-*methylaminoanthraquinone*,

$$C_6H_4{:}C_2O_2{:}C_6H_3{\cdot}NHMe,$$

which crystallises in red needles, m. p. 170° (corr.), and is soluble in warm dilute hydrochloric acid.

1-p-*Toluenesulphonylanilinoanthraquinone*,

$$C_{14}H_7O_2{\cdot}NPh{\cdot}SO_2{\cdot}C_6H_4Me,$$

crystallises from alcohol in pale yellow, felted needles, m. p. 198°, and on hydrolysis yields 1-*anilinoanthraquinone*, $C_{14}H_7O_2{\cdot}NHPh$, which can be prepared more readily by boiling 1-chloroanthraquinone with an excess of aniline, potassium acetate, and a little copper acetate and finely divided copper. It crystallises from alcohol in glistening, red plates, m. p. 147·5° (corr.). 1-p-*Nitroanilinoanthraquinone*, $C_{14}H_7O_2{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$, crystallises from nitrobenzene in red needles, m. p. 311° (corr.), and when reduced with an alcoholic solution of sodium sulphide yields 1-p-*aminoanilinoanthraquinone*, $C_{20}H_{14}O_2N_2$, which crystallises in brilliant, dark violet needles with a metallic lustre, and has m. p. 203° (corr.). Its solutions in most organic solvents are violet, its acetic acid solution is red, and its concentrated sulphuric acid solution green. The *acetyl* derivative, $C_{22}H_{16}O_3N_2$, crystallises in red needles, m. p. 176°.

1 : 1-*Dianthraquinonyl*-p-*phenylenediamine*,

$$C_6H_4[NH{\cdot}C_6H_3{:}C_2O_2{:}C_6H_4]_2,$$

crystallises from pyridine in dark violet-coloured needles with a metallic lustre, and has m. p. 328°. Its solution in concentrated sulphuric acid has a violet-blue colour.

II. [With Otto Fodor.]—*Anthraquinoneazines.*—1-o-*Nitroanilinoanthraquinone*, $C_{20}H_{12}O_4N_2$, obtained by condensing 1-chloroanthraquinone with *o*-nitroaniline or 1-aminoanthraquinone with *o*-chloronitrobenzene, crystallises from pyridine in glistening, reddish-brown prisms, m. p. 293° (corr.), and when reduced with an alcoholic solution of sodium sulphide yields *anthraquinone*-1 : 2-*dihydrophenazine*, $C_6H_4{<}{}^{NH}_{NH}{>}C_6H_2{:}C_2O_2{:}C_6H_4$, which crystallises from pyridine or nitrobenzene in glistening, blue needles, resembling indigotin; it has m. p. 310° (decomp.), after sintering at 300°. When oxidised with a mixture of glacial acetic and nitric acids, it yields *anthraquinone*-1 : 2-*phenazine*, $C_6H_4{<}{}^{N}_{N}{>}C_6H_2{:}C_2O_2{:}C_6H_4$, as yellow crystals, m. p. 253° (corr.). This dissolves in concentrated hydrochloric acid, yielding a yellowish-brown solution, and in sulphuric acid to an orange-coloured solution. When reduced with hyposulphite, it yields the dihydrophenazine, and this when boiled with acetic anhydride and potassium acetate yields 9 : 10-*diacetylanthraquinol*-1 : 2-*dihydrophenazine*, $C_6H_4{<}{}^{C(OAc)}_{C(OAc)}{>}C_6H_2{:}N_2H_2{:}C_6H_4$, in the form of glistening, yellowish-red needles, m. p. 256° (corr.). The solutions have a yellow colour with a green fluorescence. 1-o-*Aminoanilinoanthraquinone*,

$$C_6H_4{:}C_2O_2{:}C_6H_3{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2,$$

obtained by reducing the corresponding nitro-compound with an alkaline solution of sodium hyposulphite, crystallises from alcohol in

violet, felted needles, m. p. 204° (corr.), and forms a *hydrochloride* in the form of pale red needles. The *acetylamino*-compound, $C_{22}H_{16}O_3N_2$, forms small, red crystals, m. p. 257° (corr.), and is obtained by acetylating the amino-compound with acetic anhydride; if potassium acetate is also used, the product is *methyl*-1-*anthraquinonylbenziminazole*, $C_6H_4{:}C_2O_2{:}C_6H_3{\cdot}N{<}{}^{C_6H_4}_{CMe}{\geqslant}N$, which crystallises from alcohol in glistening, lemon-yellow prisms, m. p. 237°.

1-o-*Nitro*-p-*toluidinoanthraquinone*,

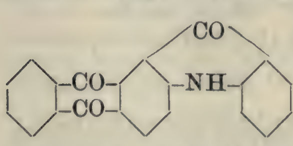
$$C_6H_4{:}C_2O_2{:}C_6H_3{\cdot}NH{\cdot}C_6H_3Me{\cdot}NO_2,$$

prepared from 1-chloroanthraquinone and *o*-nitro-*p*-toluidine in the presence of potassium carbonate, copper acetate, and nitrobenzene, crystallises from pyridine in red needles, m. p. 254° (corr.), and on reduction with sodium sulphide yields *anthraquinone* 1 : 2-*dihydro*-4′-*methylphenazine*, $C_{21}H_{14}O_2N_2$, which crystallises from pyridine or nitrobenzene in greenish-blue needles. 4′-*Chloro*-2′-*nitroanilino*-1-*anthraquinone*, $C_6H_4{:}C_2O_2{:}C_6H_3{\cdot}NH{\cdot}C_6H_3Cl{\cdot}NO_2$, crystallises in coppery-red, glistening needles, m. p. 341° (corr.), and on reduction yields *anthraquinone*-4′-*chloro*-1 : 2-*dihydrophenazine*, $C_{20}H_{11}O_2N_2Cl$. This crystallises from nitrobenzene in glistening, violet needles with a green iridescence, m. p. 310—320°.

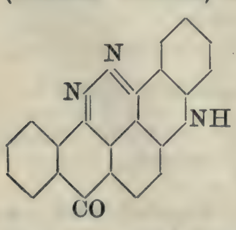
III. [With Masuo Sone.]—*Anthraquinone*-1 : 2-*acridone* (compare Abstr., 1910, i, 696).—p-*Bromobenzoylbenzoic acid*,

$$C_6H_4Br{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H,$$

obtained by condensing phthalic anhydride with bromobenzene in the presence of aluminium chloride at 50—85°, crystallises from dilute alcohol in colourless, glistening plates, m. p. 173°, and when heated for one hour at 160° with concentrated sulphuric acid yields 2-bromoanthraquinone (compare Kaufler, Abstr., 1904, i, 256), which condenses with anthranilic acid at 140—160° in the presence of amyl alcohol, potassium acetate, and small amounts of copper acetate and finely-divided copper (compare Goldberg, Abstr., 1906, i, 426; Ullmann, *ibid.*, 1903, i, 692; 1906, i, 459, 953), yielding *anthraquinone*-2-*anilino*-o-*carboxylic acid*, $C_6H_4{:}C_2O_2{:}C_6H_3{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$, in the form of orange-red, felted needles, m. p. 296° (corr.). The same acid can also be obtained by condensing 2-amino-anthraquinone with *o*-bromobenzoic acid, but the yield is only 40%. When the acid is heated with benzene and phosphorus pentachloride and then aluminium chloride added, *anthraquinone*-1 : 2-*acridone* (annexed formula) is obtained as orange-red needles, insoluble in most organic solvents.



Its solution in alcoholic sodium hydroxide has a violet colour, and that in concentrated sulphuric acid a wine-red colour. A pyridine solution of the acridone condenses with hydrazine hydrate, yielding *anthraquinone*-1 : 2-*acridonazine* (annexed formula) as orange-red needles, which dissolve in alcoholic sodium hydroxide, yielding an orange-coloured solution with a yellowish-green fluorescence. J. J. S.



Preparation of 1 : 2-Diaminoanthraquinone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 231091).—When a 1-halogen-2-aminoanthraquinone-3-sulphonic acid is boiled with aqueous ammonium hydroxide in the presence of a catalyst (such as copper), the halogen is replaced by an amino-group, and the so-obtained 1 : 2-*diaminoanthraquinone-3-sulphonic acid*, when heated with 80% sulphuric acid, is converted into 1 : 2-diaminoanthraquinone. F. M. G. M.

Preparation of Methoxyanthraquinones and their Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 229316. Compare Abstr., 1906, i, 192, 677; 1910, i, 751).—The preparation of methoxyanthraquinones by heating the corresponding nitro- or amino-anthraquinones with sodium methoxide, or a methyl-alcoholic solution of sodium hydroxide, has previously been described; it is found that halogen anthraquinones readily undergo this change, and the preparation of 1- and 2-methoxyanthraquinones from 1- and 2-chloroanthraquinones is now recorded. 1 : 8-Dichloroanthraquinone yields dark crystals of the leuco-compound of *chrysazine dimethyl ether*, which on oxidation by air (or sodium hypochlorite) and subsequent crystallisation from acetic acid is converted into golden-yellow crystals.

4-*Bromo*-1-*benzoylaminoanthraquinone*, yellowish-brown needles, soluble in concentrated sulphuric acid with a scarlet coloration, yields 1-benzoylamino-4-methoxyanthraquinone, whilst 1-*methylamino*-4-*methoxyanthraquinone*, violet prisms, was similarly obtained from 4-*bromo*-1-*methylaminoanthraquinone*.

4-*Chloro*-1-*methoxyanthraquinone*, yellow needles, obtained by chlorinating 1-methoxyanthraquinone in acetic acid solution, yields 1 : 4-*dimethoxyanthraquinone* in the form of yellow needles.

F. M. G. M.

Preparation of Arylanthraquinonylcarbamides. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 229111).—The hitherto unknown arylanthraquinonylcarbamides can be readily prepared by the action of arylcarbamides or the corresponding arylthiocarbimides on aminoanthraquinones in an indifferent solvent.

Phenyl-1- and -2-*anthraquinonylcarbamide*, yellow crystals, are obtained by boiling 1- or 2-aminoanthraquinone respectively with carbanil (3 parts) and subsequent extraction with benzene.

The action of phenylthiocarbimide (10 parts) on 2-aminoanthraquinone yields *phenyl-2-anthraquinonylthiocarbamide*, a yellow, crystalline powder, soluble in alkali with a blue coloration. F. M. G. M.

Terpenes and Ethereal Oils. CV. Reduction of Alicyclic Compounds. OTTO WALLACH (*Annalen*, 1911, **381**, 51—95).—Paal's method of reducing at the ordinary temperature with hydrogen in the presence of colloidal palladium (Abstr., 1905, ii, 397; 1907, ii, 559; 1908, i, 599; 1909, i, 358, 381, 545, 926) has been extended to the reduction of alicyclic terpene derivatives. It has the great advantage that the reduction can be accomplished under conditions such that

molecular rearrangements are practically excluded, and further brings about reductions which cannot be effected by other methods. It is shown that all unsaturated cyclic ketones, not merely those with the ethylene linking in the $\alpha\beta$-position, can be reduced by Paal's method. Thus carvone yields tetrahydrocarvone, whereas when the usual methods of reduction are used a dihydrocarvone is obtained. In the great majority of reactions the ketone is not reduced to a secondary alcohol, the process stopping at the addition of hydrogen to olefine linkings. Pinacone formation does not occur and resinous matters are not formed, so that the yields of reduced ketones are good. It is essential that the compounds to be reduced should be pure; unsaturated terpene derivatives which have been kept for some time contain substances which destroy the activity of the catalyst.

I. *Reduction of Unsaturated Cyclic Alcohols.*—*p*-Menthan-8-ol, $CH_3 \cdot C_6H_4 \cdot CMe_2 \cdot OH$, obtained by reducing inactive α-terpineol, has b. p. 209—210°, D_{20} 0·905, and n_D^{20} 1·4629. The *phenylurethane*, $C_{17}H_{25}O_2N$, crystallises from a mixture of benzene and light petroleum, or from dilute methyl alcohol, and has m. p. 117—118°. According to Behal (Abstr., 1910, i, 572) the m. p. is 94—95°, and the compound appears to exist in two stereoisomeric forms, one melting at 117° and the other at a lower temperature. The product, m. p. 94—95°, is a mixture of the two. β-Terpineol when reduced yields 1-menthanol (Baeyer, Abstr., 1903, i, 722), which has b. p. 208—209°, D^{20} 0·9000, and n_D^{20} 1·4619. The *phenylurethane* has m. p. 100—101°, and the saturated alcohol, when warmed with zinc chloride, yields a hydrocarbon, $C_{10}H_{18}$, which consists mainly of Δ^1-tetrahydro-*p*-cymene (carvomenthene). It has b. p. 174—175°, D^{21} 0·821, and n_D^{21} 1·14551, and with nitrosyl chloride yields two additive compounds. The one, $(C_{10}H_{18}ONCl)_2$, crystallises from acetone or methyl alcohol, has m. p. 95—96°, and with piperidine yields a nitrolpiperidide, m. p. 159°, from which by the elimination of hydrogen chloride a solid oxime is obtained. After this has been purified by conversion into the semicarbazone, m. p. 177—178°, an oxime identical with carvotanacetoxime, m. p. 93—94° (Abstr., 1895, i, 672), is obtained, and as carvotanacetone is readily reduced to tetrahydrocarvone, these reactions afford a method of passing from β-terpineol to tetrahydrocarvone.

Sylveterpineol (Abstr., 1907, i, 1061) on reduction yields a *m*-menthanol, $C_{10}H_{19} \cdot OH$, with b. p. 206—208°, D^{18} 0·9090, and n_D^{18} 1·4645. The *phenylurethane* has m. p. 71—74°. The position of the hydroxyl group in the reduction product has not been determined. *i*-Pinol hydrate when reduced yields a *menthandiol*, $C_{10}H_{20}O_2$, with m. p. 139—140°. According to the formula usually ascribed to pinol hydrate the reduction product should be menthan-2 : 8-diol (Rupe and Schloschoff, Abstr., 1905, i, 450), but the *d*- and *l*-modifications of this have m. p. 112—113°, and the *dl*-compound, m. p. 108—109°.

II. *Carvone Series.*—On reduction in the presence of colloidal palladium, *d*-carvone yields *l*-tetrahydrocarvone; this has b. p. 221°, D^{20} 0·9025, n_D^{20} 1·4544, and $[\alpha]_D - 20°20'$. The corresponding *oxime* has m. p. 99—100° and $[\alpha]_D - 35·7°$, and the *semicarbazone*, m. p. 193°. When small amounts of *r*-carvone are present in the

original compound, the reduction product is not homogeneous, and yields a mixture of two oximes. Tetrahydroeucarvone (Abstr., 1905, i, 451), obtained by reducing eucarvone, yields two semicarbazones, and the ketone regenerated from the less fusible product (m. p. 201°, not 191—192°) also yields a similar mixture. α-Dicarvelone (Abstr., 1899, i, 530), when reduced in aqueous acetone solution, yields *tetrahydrodicarvelone*, $C_{20}H_{34}O_2$, which crystallises from alcohol in long, flat plates, m. p. 129—130°.

Carvenolide (Abstr., 1895, i, 622; 1899, i, 532) yields *dihydrocarvenolide*, $C_{10}H_{16}O_2$, and hence contains only one olefine linking. The addition of hydrogen takes place very readily in methyl-alcoholic solution, and the product is more volatile than carvenolide in steam. It has b. p. 260—261° (uncorr.) and m. p. 36—38°. It is suggested that carvenolide is probably the lactone, $CH\!\!<\!\!\begin{matrix}CMe\cdot CH\cdot CO-\\ \quad\;\;| \\ CH_2-CH\cdot CMe_2\end{matrix}\!\!>\!\!O$, and the dihydro-derivative would then be the lactone of hydroxydihydropulegenic acid.

III. [With Erwin Meyer.]—*Reduction of Pulegenolide and of Pulegenamide.*—Pulegenolide (Abstr., 1898, i, 484) is not a saturated lactone as it yields a *dihydro*-derivative, $C_{10}H_{16}O_2$, which crystallises from dilute methyl alcohol in long, pointed needles, m. p. 49—50°, has an odour resembling that of menthone, and is accompanied by another readily fusible reduction product, which so far has not been obtained in a pure state. The amide of pulegenic acid on reduction yields a *product*, m. p. 149—150°.

IV. *Fenchone Series* (compare this vol., i, 310).—α-Fenchonitrile when reduced yields *dihydro-α-fenchonitrile*, $C_{10}H_{17}N$, with b. p. 214—215°, D^{20} 0·8730, n_D^{20} 1·4434, and α_D $-5°$ in 1-dcm. tube. α-Fencholenamide yields a *dihydro*-derivative, $C_{10}H_{19}ON$, with m. p. 134° and $[\alpha]_D$ $+4·95°$, and when dehydrated by means of phosphoric anhydride yields the corresponding dihydronitrile. The amide of β-fenchonelic acid is not reduced so readily as the isomeride, and yields as the reduction product the amide of fencholic acid; the corresponding nitrile, $C_{10}H_{17}N$, has b. p. 217—218°, D^{20} 0·8680, and n_D^{20} 1·4426.

[With Friedrich Pohle.]—*α-Dihydrofencholenic acid*, $C_{10}H_{18}O_2$, obtained by hydrolysing the corresponding amide with concentrated hydrochloric acid at 150°, has b. p. 259—260°, D^{20} 0·9740, n_D^{20} 1·4583, and α_D $+2°45'$ in a 1-dcm. tube.

V. [With Frederik Challenger.]—*Thujone Series.*—Thuja ketone is readily reduced to *dihydrothuja ketone*, $CHMe_2\cdot CHMe\cdot CH_2\cdot CH_2Ac$, the *semicarbazone* of which, $C_{10}H_{21}ON_3$, crystallises from methyl alcohol and has m. p. 152—153°. The pure ketone obtained by hydrolysing the semicarbazone with 30% sulphuric acid has b. p. 185·5—186°, D^{20} 0·8340, and n_D 1·4254. When reduced with sodium and alcohol, the saturated ketone yields *dihydrothujaketol*, $C_9H_{20}O$, with b. p. 191·5—192·5°, D^{18} 0·835, and n_D 1·4352. The *tertiary alcohol*, $CHMe_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CMe_2\cdot OH$, prepared by the action of magnesium methyl iodide on dihydrothuja ketone, is a liquid with an odour of roses, and has b. p. 192—194°, D^{18} 0·833, and n_D^{18} 1·4363.

With zinc chloride at 155°, the tertiary alcohol yields the *hydrocarbon*, $C_{10}H_{20}$, with b. p. 159·5—161°, D^{19} 0·7575, and n_D^{19} 1·4315. *δ-Acetyl-β-*iso*propylvaleric acid*, $CH_2Ac\cdot CH_2\cdot CHPr^{\beta}\cdot CH_2\cdot CO_2H$, obtained by reducing β-thujaketonic acid, is an oil and yields a *semicarbazone*, $C_{11}H_{21}O_3N_2$, with m. p. 140°. When oxidised with hypobromite, the acid yields *β-*iso*propyladipic acid*,

$$CO_2H\cdot CH_2\cdot CH_2\cdot CHPr^{\beta}\cdot CH_2\cdot CO_2H.$$

This is readily soluble in water, does not crystallise well, has m. p. 80—84°, and when its calcium salt is distilled yields 1-iso*propyl*cyclo*pentan-3-one*, $CPr^{\beta}{<}\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CH_2\end{matrix}$, the *semicarbazone* of which has m. p. 190—191°. The same ketone is formed when Semmler's tanacetophorone is reduced. Tanacetophorone semicarbazone has m. p. 187—188°, and the ketone regenerated from the semicarbazone has b. p. 212—214°, D^{20} 0·938, and n_D^{20} 1·4788. *iso*Thujone combines with hydrogen slowly and incompletely to thujamenthone.

VI. *Methylheptenone.—β-Methylheptane-ε-one* (iso*amylacetone*),

$$CHMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot COMe,$$

obtained by reducing methylheptenone, has b. p. 164—165°, D_{19} 0·8165, and n_D^{19} 1·4144. It shows no tendency to intramolecular condensation. The *semicarbazone* has m. p. 157—158° (compare Auden, Perkin, and Rose, Trans., 1899, **75**, 909).

VII. [With Friedrich Ritter].—*Preparation of* 4-*Acetyl*-1-*methyl*cyclo*hexane and its Transformation into* p-*Menthan*-8-*ol*. 4-*Acetyl*-1-*methyl*cyclo*hexane*, $C_6H_{10}MeAc$, can be prepared by the following methods: (1) Reduction of the nitrosochloride from 1-methyl-4-ethylidene*cyclo*hexane (Perkin and Wallach, Trans., 1910, **97**, 1429) with zinc dust and glacial acetic acid. (2) Reduction of an aqueous suspension of 4-acetyl-1-methyl-Δ^3-*cyclo*hexene (*loc. cit.*, 1431) with hydrogen and palladium hydrosol. (3) Reduction of the isomeric 4-acetyl-1-methyl-Δ^1-*cyclo*hexene with hydrogen and palladium. The last method is the most economical, and the product has b. p. 195—197°, D_{18} 0·9055, n_D^{18} 1·4509. The *semicarbazone*, $C_9H_{16}{:}N\cdot NH\cdot CO\cdot NH_2$, does not crystallise at all readily, and has m. p. 159°. A specimen which had been kept for several months crystallised from methyl alcohol in well-developed needles, and had m. p. 175°. The *oxime*, $C_9H_{17}ON$, has m. p. 57—59° and b. p. 125—130°/15 mm. The *secondary alcohol*, $C_6H_{10}Me\cdot CHMe\cdot OH$, obtained by reducing the ketone with sodium and alcohol, is a liquid with a pleasant odour and b. p. 96°/15 mm. The *phenylurethane* crystallises from methyl alcohol and has m. p. 62—63°. 1-Methyl*cyclo*hexane-4-carboxylic acid (hexahydro-*p*-toluic acid: Perkin and Pickles, Trans., 1905, **87**, 1639) is formed when the ketone is oxidised with hypobromite. *p*-Menthan-8-ol can be synthesised by the action of the Grignard reagent on the saturated ketone.

VIII. *Reduction of Unsaturated Alicyclic Acids.*—The two isomeric *cyclo*hexeneacetic acids (Abstr., 1907, i, 616) and the isomeric 1-methyl*cyclo*hexene-4-acetic acids (*ibid.*, 1906, i, 566; 1907, i, 618) are readily reduced by hydrogen and palladium to the corresponding saturated acids. J. J. S.

Terpenes and Ethereal Oils. CVI. Dicyclic Compounds from *cyclo*Hexanone. OTTO WALLACH (*Annalen*, 1911, **381**, 95—113).—I. [With ALEXANDER WACKER and FRIEDRICH PAULY.]—cyclo*Hexenhexanone* and cyclo*Hexenhexanol.* — The constitutional formula previously ascribed to *cyclo*hexene-2-*cyclo*hexanone (Abstr., 1907, i, 220) is confirmed.

The ketone has b. p. 273—275°, D_{18} 1·005, and n_D^{18} 1·5082. Its *semicarbazone* has m. p. 179—181°. The corresponding unsaturated alcohol has m. p. 34—35°, b. p. 272—273°, D_{37} 0·974, and n_D^{37} 1·5007. Its *phenylurethane*, $C_{19}H_{25}O_2N$, has m. p. 118—119°. The same alcohol is formed when sodium is added to a boiling solution of *cyclo*hexanone in toluene. When carefully oxidised with chromic acid, it yields the *cyclo*hexene-*cyclo*hexanone, but when a benzene solution of the alcohol is oxidised at 0° with 2% permanganate the products are a *trihydric alcohol*, $C_{12}H_{19}(OH)_3$, b. p. 202—205°/10 mm., but mainly the *ketonic acid*, $C_6H_9\cdot CO\cdot[CH_2]_4\cdot CO_2H$. The acid crystallises from benzene in yellow needles, m. p. 74—75°, yields a *semicarbazone*, $C_{13}H_{21}O_3N_3$, m. p. 190—200°, and with hydrogen chloride forms an additive *compound*, $C_{12}H_{19}O_3Cl$, which crystallises from light petroleum in plates, m. p. 48—51°. The ketonic acid is not formed when the original ketone is oxidised, but can be obtained from the *oxime* of the ketone. This has m. p. 146—151°, and on reduction yields bicyclo*hexenhexylamine*, $C_{12}H_{19}NH_2$, m. p. 33—35°, which is oxidised by permanganate to the ketonic acid.

II. [With WALTER OST.]—cyclo*Hexyl*cyclo*hexanone.*—*cyclo*Hexene-*cyclo*hexanone is reduced in methyl-alcoholic solution by hydrogen and palladium to the corresponding saturated ketone, cyclo*hexyl*-2-cyclo*hexanone*, $CH_2{<}^{CH_2\cdot CH(C_6H_{11})}_{CH_2\text{———}CH_2}{>}CO$. This has b. p. 137°/12 mm., D_{18} 0·978, and n_D^{18} 1·4887. The *semicarbazone* has m. p. 203°; the *oxime*, $C_{12}H_{21}ON$, m. p. 100°, and the *benzylidene* derivative, $C_{19}H_{24}O$, crystallises from alcohol in glistening plates, m. p. 100°. When reduced with sodium and alcohol the saturated ketone yields 2-cyclo*hexyl*cyclo*hexanol*, $C_6H_{11}\cdot C_6H_{10}\cdot OH$, with b. p. 264° (uncorr.) and m. p. 42°. The *phenylurethane* has m. p. 117°. 2-cyclo*Hexyl*-Δ^1-cyclo*hexene*, $C_6H_{11}\cdot C_6H_9$, formed when the saturated alcohol is heated with zinc chloride, has b. p. 237°, D_{20} 0·9010, n_D^{20} 1·4910. Its *nitrosochloride* has m. p. 140°, and resembles *cyclo*hexene nitrosochloride. When oxidised with an acetic acid solution of chromium trioxide, the saturated ketone yields *δ-hexahydrobenzoyl*-n-*valeric acid*, $C_6H_{11}\cdot CO\cdot[CH_2]_4\cdot CO_2H$, which crystallises from a mixture of ether and light petroleum. It has m. p. 58°, and yields a *semicarbazone*, which crystallises from methyl alcohol in needles, m. p. 172—173°. The *oxime*, $C_{12}H_{21}ON$, has m. p. 105°, and the *methyl* ester of the acid, b. p. 173°/13 mm., D_{18} 1·0175, and n_D^{18} 1·4658.

The same acid can be obtained by reducing the unsaturated ketonic acid (m. p. 74—75°) with hydrogen in the presence of colloidal palladium. The acid itself is not affected by chromic acid, by hydrogen chloride at 100°, or by dilute sulphuric acid at 160°, but the methyl ester reacts with metallic sodium in the presence of

toluene at 120°, and finally at 130°, yielding 1-*hexahydrobenzoyl-2-pentanone*, $C_6H_{11}\cdot CO\cdot CH<\begin{matrix}CO-CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}$, which, after purification by conversion into its *copper* salt, forms a colourless liquid, b. p. 150°/11 mm. The ketone does not yield a semicarbazone or oxime, and cannot be hydrolysed to *cyclo*hexanecarboxylic acid and *cyclo*pentanone. When boiled with sodium hydroxide solution it yields the original ketonic acid, m. p. 58°, and when methylated yields a *methyl* derivative, $C_{13}H_{20}O_2$, which gives a *semicarbazone*, $C_{14}H_{23}O_2N_3$, m. p. 203°.

The *hydroxy-acid*, $C_{12}H_{22}O_3$, obtained by reducing the ketonic acid with sodium and alcohol, forms a thick syrup, and when distilled under reduced pressure yields the *lactone*, $C_{12}H_{20}O_2$, m. p. 45°, which reacts with sulphuric acid (1 : 1·5), yielding an unsaturated *acid*, $C_{12}H_{20}O_2$, with b. p. 182—186°/20 mm. When fused with potassium hydroxide and a little water at 230°, the saturated ketonic acid yields a sparingly volatile, unsaturated acid, m. p. 172°.

III. [With Friedrich Pauly.]—$\Delta^{1:1'}$-*Di*cyclo*hexene*.—Di*cyclo*hexyl-1 : 1′-diol (*cyclo*hexane-pinacone : Zelinsky, Abstr., 1901, i, 683) when boiled with dilute sulphuric acid yields $\Delta^{1:1'}$-*di*cyclo*hexene*,

$$CH_2<\begin{matrix}CH_2-CH\\ CH_2\cdot CH_2\end{matrix}>C\cdot C<\begin{matrix}CH_2\cdot CH_2\\ CH-CH_2\end{matrix}>CH_2,$$

as a colourless liquid with b.p. 120—125°/15 mm. or 250—253°/760 mm., D_{20} 0·9485, and n_D^{20} 1·5287. The *dihydrobromide*, $C_{12}H_{20}Br_2$, crystallises from methyl alcohol in colourless needles, m. p. 68—69°.

*Dimethyldi*cyclo*hexene*, obtained from 1-methyl-3-*cyclo*hexanone, has b. p. 265—267°. J. J. S.

Action of Ethyl Iodide and Magnesium on Menthone and Carvone. Ivan Vanin (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 353).—The action of ethyl iodide and magnesium (or zinc) on menthone yields a *hydrocarbon*, $C_{12}H_{22}$, b. p. 195—197°. The action of ethyl iodide and magnesium (or zinc) on carvone yields an *alcohol*, $C_{12}H_{20}O$, b. p. 248—253°, which, on oxidation, gives a trihydric alcohol.

T. H. P.

Action of Zinc on a Mixture of Menthone and Allyl Iodide. Michael Saytzeff (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 329—344).—By the action of zinc on a mixture of menthone and allyl iodide, the author has obtained 1-methyl-4-*iso*-propyl-3-allyl*cyclo*hexan-3-ol, or 3-allylmenthan-3-ol (compare Javorsky, Abstr., 1909, i, 168; Ryschenko, Abstr., 1910, i, 181), D_4^{20} 0·90794, n_a^{20} 1·47234, n_D^{20} 1·475, n_β^{20} 1·48145, $[\alpha]_D^{20}$ −56°13′48″, b. p. 246—252°.

Oxidation of the alcohol proceeds in two different directions according to the conditions employed. With 1% permanganate solution in the proportion corresponding with 1 atom of oxygen per mol. of the alcohol, the latter yields the *trihydric alcohol*,

$$CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2\cdot CHPr^\beta\end{matrix}>C(OH)\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH,$$

whilst a more concentrated solution of permanganate (40 per mol. of alcohol) yields oxalic acid and the *acid*,

$$CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2\cdot CHPr^\beta\end{matrix}>C(OH)\cdot CH_2\cdot CO_2H,$$

of which the *calcium*, *silver*, *barium*, and *zinc* salts were prepared. The action of bromine on 1-methyl-4-*iso*propyl-3-allyl*cyclo*hexan-3-ol gives the *dibromide*, $C_{13}H_{24}OBr_2$, as a viscous, brown, unstable liquid.

The action of hydrogen chloride or bromide on 1-methyl-4-*iso*propyl-3-allyl*cyclo*hexan-3-ol in the cold gives the corresponding *chloro-*, $C_{13}H_{23}Cl$, or *bromo*-derivative, $C_{13}H_{23}Br$. When either of these compounds is treated with alcoholic potassium hydroxide, it yields the *hydrocarbon*, $CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2\cdot CHPr^\beta\end{matrix}>C:CH\cdot CH:CH_2$ or

$$CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2-CPr^\beta\end{matrix}\gg C\cdot CH_2\cdot CH:CH_2,$$

b. p. 212—218°, which takes up bromine, giving the *compound*, $C_{13}H_{22}Br_4$, as a viscous, brown liquid. T. H. P.

Some Derivatives of Dicamphor. Giuseppe Oddo (*Gazzetta*, 1911, **41**, i, 126—131).—A criticism of the work of Castellana and Ferrero (this vol., i, 217), principally as regards nomenclature.

T. H. P.

Constituents of Ethereal Oils. Enolisation of Citral; Preparation of *iso*Geraniol, $C_{10}H_{18}O$. Friedrich W. Semmler and E. Schossberger (*Ber.*, 1911, **44**, 991—995).—Aldehydes containing labile hydrogen atoms are converted on boiling with acetic anhydride and sodium acetate into enolic acetates. In the case of citral such process would lead to the formation of a carbon atom with two double bonds, but one of these wanders to the conjugated position, and the physical data of the compound obtained point to this being to the CH_2- rather than to the CH_3-group. enol-*Citral acetate*, $C_9H_4:CH\cdot OAc$, has b. p. 118—126°, D^{20} 0·942, n_D 1·501, and a high molecular refraction. It is reduced by sodium amalgam and methyl alcohol to iso*geraniol*, isomeric with geraniol and nerol, having b. p. 102—103°/9 mm., D^{20} 0·879, n_D 1·473, and an odour of roses. The *diphenylurethane* has m. p. 73°; the *phenylurethane* and *tetrabromide* are oily. E. F. A.

Essential Oils. Schimmel & Co. (*Bericht*, April 1911, pp. 1—208). —*Andropogon* (*Cymbopogon*) *Schoenanthus* var. *nervatus* from the Sudan furnished 1·9% of a brown oil, D^{15} 0·9405, α_D + 26°22′, n_D^{20} 1·49469, acid number 4·6, ester number 9·3, acetyl ester number 99·1, which resembled gingergrass oil in odour, and was soluble in 0·5 or more volumes of 80% alcohol, but deposited a paraffin when further diluted.

Cananga oil from Java had D_4^{25} 0·9068—0·9108, α_D − 20·3° to − 21·8°, n_D^{40} 1·4906 to 1·4919, saponification number 24·2—28·4, and was soluble with slight opalescence in 96% alcohol.

The wood of *Cinnamomum Parthenoxylon* gave a yellow oil having D^{15} 1·0799, α_D + 1°22′, n_D^{20} 1·53229, which was soluble in 2·6 vols. or more of 90% alcohol and had a strong odour of safrole.

Investigations carried out at the Imperial Institute have shown that the citronella grasses of Ceylon are of four kinds, namely: (1) *Cymbopogon Nardus*, Rendle var. *Linnaei*, Stapf (*typicus*); (2) *C. Nardus*, Rendle var. *confertiflorus*, Stapf; (3) *C. Nardus*, Rendle, *lenabatu*, and (4) *C. Winterianus*, Jowitt, the first two being wild and the last two cultivated varieties. Sixteen samples of oil prepared from different specimens of the first variety have been examined, and, omitting two which exhibited certain irregularities, these show the following range of constants: D^{15} 0·894—0·926, α_D + 4°54′ to − 6°32′, and "total alcohols" 43·5—64·7%. Nine samples of oil prepared from different specimens of the second variety had D^{15} 0·900—0·929, α_D + 12°12′ to − 2°11′, and "total alcohols" 39·1—64·2%. The yield of oil from these wild grasses was 0·06—0·45%. The oils from the two cultural varieties resembled common citronella oil from Ceylon and Java respectively (compare *Bull. Imp. Inst.*, 1910, **8**, 144, and *Agric. Journ. Bot. Gard. Ceylon*, 1910, **5**, 115).

The fruit rinds of *Citrus Hystrix* from Java furnished 4% of yellow oil, D^{26} 0·942, α_D + 9°, containing 40% of citral.

Turmeric roots furnished 3·23% of a golden-yellow oil, D^{15} 0·9430, α_D − 23°, n_D^{20} 1·51236, acid number 1·6, ester number 7·8, acetyl ester number 30·0, which gave a marked reaction for phellandrene (compare Bacon, Abstr., 1911, i, 73).

Cymbopogon coloratus oil from Fiji had D^{15} 0·920, contained 42% of aldehydes and 15% of geraniol, and had an odour recalling those of lemongrass and citronella oils (compare *Bull. Imp. Inst.*, 1910, **8**, 145).

C. Jwarancusa (?) from the Sudan furnished an oil, which resembles pennyroyal oil in odour, and consists principally of an aromatic ketone (*loc. cit.*).

C. polyneuros oil from Ceylon gave 0·20—0·34% of yellow to reddish-brown oil, D^{15} 0·936—0·951, α_D + 30°53′ to + 55°15′, which was soluble in 1 vol. of 80% alcohol, and contained 38·7—51·8% of "total alcohols" (*loc. cit.*).

Warburgia Stuhlmanni bark furnished 0·6% of a viscous, yellowish-red oil, D^{20} 0·9864, α_D^{20} − 41·2°, n_D^{20} 1·51269, saponification number 11·2, acetyl ester number 111·5, which is miscible with anhydrous alcohol, has an odour recalling that of sandalwood oil, and contains an aldehydic constituent and some sulphur compounds.

Andropogon (*Cymbopogon*) *citratus* roots from Java gave an oil, α_D − 1°40′, containing 82% of citral, whilst the rhizomes yielded an oil, D^{20} 0·94, α_D − 3°40′, containing 11% of citral.

The leaves and twigs of *Melaleuca trichostachya* furnish, according to Baker and Smith, 2·5% of oil containing 85—95% of cineol, whilst, according to the same authors, *M. bracteata* leaves and twigs furnish 1% of oil containing methyleugenol, cinnamaldehyde, and free and combined cinnamic acid.

Monarda citriodora, according to Lefebvre and Wakeman, furnishes an oil, D^{15} 0·9603, containing phenols 72%, and aldehydic substances 4%. The non-phenolic portion contains 16·98% of alcohols.

The bark of *Myristica fragrans* from Java gave 0·14% of oil, D^{26} 0·871, having a rotation − 12°14′ in a 10 cm. tube.

Origanum oil from Greece had $D^{15.5}$ 0·9351, α_D $\pm 0°$, n_D^{22} 1·502, contained 63% of phenols, and was soluble in four or more volumes of 70% alcohol.

Mentha canadensis var. *piperascens*, grown in Germany, furnishes, according to Thoms, a peppermint oil very similar to Japanese peppermint oil. Irk's examination of Hungarian peppermint oil shows that this closely resembles American peppermint oil.

Prunus sphaerocarpa bark, according to Peckolt, furnishes 0·046% of oil, D^{18} 1·0409, which has an odour of bitter almond oil. Amygdalin was isolated from the seeds of the same plant, whilst the leaves furnished from 0·0016% (in winter) to 0·085% (in summer) of hydrogen cyanide.

The fraction of savin oil boiling at 170—180° contains α-terpinene.

Majorana Onites from Smyrna gave 2% of dark brown oil, D^{15} 0·9572, α_D $-1°30'$, which contained 74% of phenols, principally carvacrol. The non-phenolic portion contained α-pinene, *p*-cymene, *l*-linalool, and *d*-camphor, with one or more sesquiterpenes.

Indian turpentine oil contains α-pinene, β-pinene, sylvestrene, and a *sesquiterpene*, D^{15} 0·9371, α_D $+37°4'$, n_D^{20} 1·50252, which furnishes a *hydrochloride*, m. p. 59·5—60·5°, crystallising in long needles (see also *Bull. Imp. Inst.*, 1911, **9**, 9).

Thymus mastichina, according to Dorronsoro, furnishes an oil D_{15}^{20} 0·907—0·945, α_D $-0°50'$ to $+4°40'$, n_D^{23} 1·4630 to 1·4654, saponification number 12·7—18·5, and acetyl ester number 29·2 to 49·3, which contains *d*-α-pinene 7—8%, cineol 64—72%, phenols and ketones less than 0·1%, linalyl acetate 4·4—6·4%, and free alcohols 8·2—14·1%, with small quantities of free and combined acetic and *iso*valeric acids.

Balan oil from Java, D^{15} 0·9042, n_D^{20} 1·47715, acid number 13·0, ester number 20·5, which is used in native medicine as a vermifuge, furnished on extraction with sodium hydrogen sulphite solution a product from which a *semicarbazone*, m. p. 152°, was obtained.

Eugenia occlusa leaves gave 0·05% of dark brown oil, D^{15} 0·9567, α_D $-1°40'$, n_D^{20} 1·48614, which deposits paraffin (?) at 12° and contains citral and other aldehydes.

The cones of *Pinus excelsa* from India yielded a yellow oil, D^{15} 0·8757, α_D $-32°45'$, n_D^{20} 1·47352, acid number 0·5, ester number 5·6 (corresponding with 2·0% of bornyl acetate), which was soluble in five or more volumes of 90% alcohol.

A résumé is also given of recent work on the botany, pharmacology, analysis, chemistry, and physical constants of essential oils.

T. A. H.

The Pines of Australia. RICHARD T. BAKER and HENRY GEORGE SMITH (*Technical Education Series, Technological Museum, New South Wales*, 1910, No. 16, p. 1—458).—The morphology, anatomy, physiology, and chemistry of the principal genera of the Coniferæ, occurring in Australia and Tasmania, have been studied with a view to (1) their more exact botanical classification, (2) the determination of their economic importance as sources of resins, volatile oils, timbers, and other products. The genera dealt with are *Callitris*,

Actinostrobus, *Diselma*, *Microcachrys*, *Athrotaxis*, *Araucaria*, *Agathis*, *Dacrydium*, *Pherosphaera*, *Phyllocladus*, and *Podocarpus*. The following are the chief general results of chemical interest obtained: (1) A sequence of *Callitris* species is outlined, based in part on the composition of the leaf oils obtained from them; (2) a relationship is shown to exist between the anatomical characters of *Callitris* leaves and the composition of the oils they furnish, and (3) a number of new facts relating to the composition and characters of the volatile oils, resins, etc., furnished by the species studied are recorded.

The oils yielded by the leaves of *Callitris* species are mostly dextrorotatory and generally colourless, but become acid on keeping. They contain *d*- and *l*-pinene, *d*- and *l*-limonene, sesquiterpenes, *d*-borneol, and geraniol and terpineol, as their acetic esters, and terpineol and an ester of this, probably the butyrate. In a few cases traces of phenols are present. The sesquiterpenes are present in small amount as a rule. The other constituents all reach a maximum in the leaves of one species. In *C. Drummondii* leaf oil *d*-pinene is at a maximum, in *C. Muelleri* *l*-pinene, in *C. arenosa* *d*-limonene, in *C. intratropica* *l*-limonene, in *C. Tasmanica* geranyl acetate, and in *C. gracilis* terpineol. Though the leaf oils practically all contain the same constituents, yet the amounts of these present vary with each species, so that the composition of the oil is often enough to determine its botanical source. The principal constants and constituents of the oil from each species are given in detail in the original: those for *C. Macleayana* leaf oil are D^{20} 0·8484, $[\alpha]_D$ +42·5°, n_D 1·4791, esters 3·5%. This oil differs considerably from *Callitris* leaf oils in general; it contains *d*-pinene, *d*-limonene, dipentene, a sesquiterpene (cadinene?), a small quantity of esters, and a large proportion of a hydrocarbon, $C_{10}H_{18}$, which may be *d*-menthene.

The constituents of the oils from the fruits of *Callitris* species, as a rule, are the same as those of the leaf oils of the same species, but the terpenes present are often of opposite optical activity.

The wood of *Callitris glauca* yields 0·82% of volatile oil, which is semi-solid owing to the separation of guaiol. The liquid portion, which still contains guaiol, has D^{16} 0·9854, acid number 68·8, and saponification number 106·6, and distils as follows: 60% from 248—255°, 21% from 255—265°, and 10% from 266—296°. The first fraction is largely sesquiterpene, D^{15} 0·9266, n_D^{15} 1·4926, and b. p. 250—252°. The second and third fractions are dark blue in colour. On saponification and separation of guaiol the liquid portion furnishes a *phenol*, which also occurs free in the oil. This is a viscous oily substance giving with acetic acid and bromine a characteristic purple coloration, which changes to blue. It is proposed to call this phenol *callitrol*. Both guaiol and callitrol occur in other *Callitris* timbers.

The barks of *Callitris* species all appear to contain tannins of the catechol group; the richest are the barks of *C. calcarata* and *C. arenosa*, which may contain up to 36 and 34% respectively. The specific rotations and relative solubilities of the resins of *Callitris* spp. are recorded.

Actinostrobus pyramidalis leaves furnish 0·256% of oil, D^{15} 0·8726,

$[\alpha]_D+40{\cdot}9°$, n_D^{19} 1·4736, which differs from *Callitris* oils in containing no limonene, but *d*-pinene and geranyl acetate are present.

Athrotaxis selaginoides leaves yield 0·076% of volatile oil, D_{15}^{16} 0·8765, $[\alpha]_D+74{\cdot}8°$, n_D^{16} 1·4905, containing *d*-limonene, pinene (?), sesquiterpene (? cadinene), carvacrol (?), and a small quantity of esters.

Araucaria Cunninghamii leaves give 0·005% of oil, D^{21} 0·8974, n_D^{21} 1·4977, consisting mainly of high boiling terpenes with a small quantity of esters. The bark contains a catechol tannin. The exudation from wounded stems of this species is an oleo-gum resin. The oil, D_{15}^{22} 0·80577, n_D^{22} 1·457, $[\alpha]_D$ + 3·2° has an odour recalling that of menthene, and consists largely of a *hydrocarbon*, $C_{10}H_{20}$, b. p. 151—153°, with some unsaturated hydrocarbons, probably of the menthane group. The aqueous portion of the distillate is acid and contains acetic and butyric acids. The gum resembles "gum arabic"; it furnishes mucic acid on oxidation with nitric acid, and arabinose on hydrolysis with acids. The resin has acid number 107, and can be separated by treatment with ether into (1) *dundathic acid*, $C_{21}H_{32}O_3$, m. p. 234—235°, $[\alpha]_D$ +55°, and (2) an *isomeride* of abietic acid, $C_{20}H_{30}O_2$, m. p. 90—91°, $[\alpha]_D$ −11·25°, and (3) a *bitter* substance. The exudation also contains protein, water, and impurities. The exudation of *A. Bidwilli* also contains gum, resin, and volatile oil, but the two latter are present in very small proportions. The oleo-resin of *Agathis robusta* contains resin 62·0%, volatile oil 11·64%, and small quantities of gum, reducing sugar, nitrogenous matters, and acetic and butyric acids. The volatile oil, D_{15}^{16} 0·8629, $[\alpha]_D$ +20·2°, n_D^{16} 1·476, consists principally of *d*-pinene.

The resin consists of (1) dundathic acid (see above); (2) *dundatholic acid*, $C_{19}H_{28}O_3$, m. p. 101—102°, $[\alpha]_D$ +21·5° in alcohol, which is amorphous, and (3) a bitter resin.

Dacrydium Franklini leaves yield 0·5% of oil, D_{15}^{17} 0·8667, $[\alpha]_D$ +20·5°, n_D^{25} 1·4815, containing the methyl ether of eugenol, *d*-limonene, *l*-pinene, and *dacrydene*, $C_{10}H_{16}$, D_0^{22} 0·8524, $[\alpha]_D$ +14·48°, n_D^{22} 1·4749, b. p. 165—166° (corr.), having a turpentine-like odour and giving a *nitrosochloride*, m. p. 120—121°, and a liquid *tribromide*. The wood yields 0·56% of oil, D_{15}^{18} 1·035, $[\alpha]_D$ +1·4°, n_D^{23} 1·5373, consisting chiefly of methyleugenol with some sesquiterpene (cadinene ?).

Pherosphaera Fitzgeraldi leaves contain 0·108% of oil, D_{15}^{22} 0·8705, $[\alpha]_D$ +15·1°, n_D^{23} 1·4841, containing *d*-pinene, limonene (?), cadinene, an aldehydic substance, and a small quantity of esters.

Phyllocladus rhomboidalis leaves (phylloclades) furnish 0·215% of oil, D^{16} 0·8892, $[\alpha]_D$ −12·3°, n_D^{16} 1·4903, which contains *l*-pinene, a *sesquiterpene*, D^{24} 0·9209, $[\alpha]_D$ +3·4°, and n_D^{23} 1·5065, a small quantity of an alcohol, and a diterpene, *phyllocladene*, m. p. 95°, $[\alpha]_D$ +16·06° in chloroform, which crystallises from alcohol in nacreous, colourless tablets and appears to be a saturated substance. It is suggested that phyllocladene is formed from 2 mols. of pinene.

In various parts of all the Australian Coniferæ studied, a brown, bronze-coloured substance containing manganese was observed microscopically and the ashes from these contained manganese. Manganese was also found in association with the gum in the exudations of *Araucaria Cunninghamii* and *Agathis robusta*. T. A. H.

Saponin from Trevesia Sundaica Leaves. J. FLIERINGA (*Arch. Pharm.*, 1911, **249**, 161—173; *Pharm. Weekblad*, 1911, **48**, 433—439).—A description is given of the method of isolation of crude saponin from this material and of its resolution into five different fractions, the principal properties and reactions of which are detailed.

An alcoholic extract of the leaves was concentrated, dissolved in very dilute alcohol, freed from fat by extraction with ether, heated under reduced pressure to remove alcohol and ether, and the saponin salted out with ammonium sulphate. This crude saponin possessed hæmolytic properties, and was precipitated from aqueous solution by basic lead acetate, whilst lead acetate only removed brown impurities. By treatment with magnesium hydroxide, it was separated into (1) green saponin, and (2) yellow saponin, the former strongly hæmolytic, the latter scarely so. The yellow saponin by solution in alcohol and fractional precipitation with ether gave four fractions, the first three amorphous, the fourth crystalline. All four fractions differed in physical properties, in the facility with which they were salted out by magnesium sulphate, and in composition. All were glucosides, and furnished sapogenin and sugars on hydrolysis by acids. Under these conditions fractions 1, 2, and 3 furnished a hexose (? dextrose), a pentose (? arabinose), and a methylpentose, whilst fraction 4 gave only the hexose and pentose. On hydrolysis with potassium hydroxide solution, fraction 1 furnished an amorphous acid glucoside, which was strongly hæmolytic, gave a crystalline potassium salt, and on further hydrolysis by acids yielded sapogenin and methylpentose, with small quantities of a pentose and hexose.

T. A. H.

Preparation of Aloin Derivatives. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 229191).—*Aloin carbonate*, a brownish-yellow, tasteless powder, is prepared by treating a cooled pyridine solution of anhydrous aloin with carbonyl chloride; after remaining some time at the ordinary temperature, water is added, the pyridine removed with dilute sulphuric acid, and the product washed with alcohol.

Aloin ethyl carbonate, a green, tasteless powder, is prepared in a similar manner with ethyl chloroformate; and *aloin allophanate*, a brownish-yellow powder, by means of carbamide hydrochloride in benzene solution.

F. M. G. M.

Colour and Constitution. BRONISLAW PAWLEWSKI (*Ber.*, 1911, **44**, 1103—1104).—An example is given of the influence of the relative positions of chromophoric and auxochromic groups on the colour of compounds. The nine azomethine compounds obtained by condensing each of the three aminobenzoic acids with each of the three nitrobenzaldehydes contain the chromophore, $\cdot N{:}CH\cdot$, in a fixed position, whilst the positions of the auxochromic CO_2H group and the chromophoric NO_2 group vary in the different substances. In the three derivatives of anthranilic acid the colour is more intense the nearer the CO_2H and the NO_2 groups are to one another; in the derivatives of the other two aminobenzoic acids the converse is the case.

C. S.

Action of Amines on Triphenylcarbinol and Tritolylcarbinol. ARTHUR G. GREEN and ARTHUR E. WOODHEAD (*7th Intern. Congr. App. Chem.*, 1909, Sect. IV B, 89).—On heating triphenylcarbinol with aniline and aniline hydrochloride for ten or twelve hours at 180°, a deep blue mass is obtained, from which only a small quantity of dye can be isolated, the main product being aminotetraphenylmethane. The properties of the dye correspond with those of a substance of the induline class, so that no introduction of a phenylimino-group seems to occur, and the triphenylcarbinol merely acts as an oxidiser on the aniline. This is confirmed by the fact that when *p*-toluidine is substituted for aniline no colour is produced. *o*-Toluidine gives a red similar to magenta, and dimethylaniline a violet like methyl-violet. Tri-*p*-tolylcarbinol reacts similarly with the amines mentioned. In all cases the yield of dye is small. R. V. S.

Action of Magnesium Thienyl Iodide on Allyl Bromide. E. GRISHKEWITSCH-TROCHIMOWSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 201—203. Compare Thomas, Abstr., 1908, i, 360).—2-*Allylthiophen*, $\begin{matrix}CH—S\\ \| \\ CH\cdot CH\end{matrix}\!\!>\!C\cdot CH_2\cdot CH\!:\!CH_2$, obtained by the interaction of allyl bromide, magnesium, and 2-iodothiophen, is a colourless, mobile liquid, b. p. 158·5—159°/732 mm., $D_4^{20\cdot5}$ 1·0175, $n_D^{20\cdot5}$ 1·52813. It decolorises bromine, and combines almost quantitatively with liquid nitrogen dioxide, giving a brownish-black, indistinctly crystalline product. With an acetic acid solution of 2-allylthiophen, phenanthraquinone dissolved in sulphuric acid gives a reddish-brown coloration, whilst, under similar conditions, isatin gives a cinnamon-red coloration. When oxidised with permanganate, 2-allylthiophen yields thiophen-2-carboxylic acid, m. p. 125—126°. T. H. P.

New Method of Preparation of, and Certain Derivatives of, Thiophen-2-aldehyde. E. GRISHKEWITSCH-TROCHIMOWSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 204—207).—The interaction of ethyl orthoformate and magnesium thienyl iodide yields the acetal,

$$\begin{matrix}CH—S\\ \| \\ CH\cdot CH\end{matrix}\!\!>\!C\cdot CH(OEt)_2,$$

which, on hydrolysis, is converted into thiophen-2-aldehyde (compare Biedermann, Abstr., 1886, 536, 870; Hantzsch, Abstr., 1890, 129).

The *acetal*, $C_9H_{14}O_2S$, is a colourless, mobile liquid, b. p. 222·5—223·5°/748 mm. (corr.), D_4^{17} 1·0571, n_D^{17} 1·49020.

The action of alcoholic ammonia on thiophen-2-aldehyde yields the *hydramide*, $C_4SH_3\cdot CH(N\!:\!CH\cdot C_4SH_3)_2$, in colourless, shining, crystalline rosettes, m. p. 111·5°. T. H. P.

[Preparation of a "Chlorothioindigo."] GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 230308).—A continuation of previous work on the production of dyes in the "thioindigo" series.

"Chlorothioindigo," m. p. 245—260°, a dark violet-coloured powder, crystallising from nitrobenzene in needles, is prepared by passing chlorine into a nitrobenzene suspension of thioindigo in the presence of a halogen carrier, such as antimony pentachloride. F. M. G. M.

Angostura Alkaloids. JULIUS TRÖGER and H. RUNNE (*Arch. Pharm.*, 1911, 249, 174—208).—In a previous paper (Tröger and Müller, Abstr., 1910, i, 414) it was shown that Angostura bark contains, in addition to amorphous alkaloids, cusparine, galipine, cusparidine, galipidine, cuspareine, and a new alkaloid, now named galipoidine; the second and fourth of these were characterised and their oxidation studied. In the present paper cusparine, cuspareine and galipoidine are dealt with, and it is shown especially that cuspareine should be represented by the formula $C_{18}H_{19}O_2N$ instead of $C_{34}H_{36}O_5N_2$ (Beckurts and Frerichs, Abstr., 1904, i, 84) or $C_{35}H_{44}O_3N_2$ (Müller, *Apoth. Zeit.*, 1909, No. 73). Galipine and galipidine are probably dihydro-derivatives of cusparine and cusparidine respectively.

The various melting points ascribed by different authors to cusparine, $C_{20}H_{19}O_3N$ (Körner and Böhringer, Abstr., 1884, 341; Beckurts and collaborators, Abstr., 1892, 642; 1896, i, 66; 1904, i, 84, and Müller, *loc. cit.*), are due to the fact that the base exists in two forms: (*a*) colourless needles, m. p. 90—91°, and (*b*) amber-coloured crystals, m. p. 110—122°. Both forms yield the same platinichloride, $B_2,H_2PtCl_6,3H_2O$, which crystallises in glancing, yellow needles, sinters at 197°, and melts at 210°.

The nitro-base prepared by Beckurts and Frerichs (Abstr., 1904, i, 84) from cusparine has the formula $C_{17}H_{14}O_4N_2,H_2O$, m. p. 142·5—143°, contains one methoxyl group like the parent base and furnishes a crystalline *nitrate*, B,HNO_3,H_2O, m. p. 168°, yellow needles; *hydrochloride*, B,HCl,H_2O, m. p. 149° (decomp.); *sulphate*, $B_2,H_2SO_4,4H_2O$, yellowish-white needles, m. p. 120°; *platinichloride*, B_2,H_2PtCl_6, m. p. 204°; *aurichloride*, $(B,HCl)_2,AuCl_3$, m. p. 200°; and *methiodide*, small, yellow needles, decomposing at 105°. On reduction, the nitro-base gives the corresponding *amino*-compound, $C_{17}H_{16}O_2N_2$, m. p. 205—206°, which crystallises in colourless needles and yields a crystalline *hydrochloride*, B,2HCl, m. p. 224° (decomp.), *platinichloride*, B,H_2PtCl_6, m. p. 248° (decomp.), and *mercurichloride*, $B,2HCl,HgCl_2$, m. p. 231° (decomp.). The sulphate on diazotisation furnishes a crystalline *substance*, which gives a *platinichloride*, m. p. 220° (decomp.), crystallising in broad prisms. On adding β-naphthol to an aqueous solution of the diazo-substance, a red *azo-dye*,

$$C_{17}H_{14}O_2N{:}N\cdot C_{10}H_6\cdot OH,C_2H_5\cdot OH,$$

m. p. 206°, is produced, which crystallises from alcohol in iridescent needles.

When heated in a closed vessel with dilute nitric acid, cusparine furnishes a *product*, $C_5H_5O_5N_3$, crystallising in brownish-yellow needles.

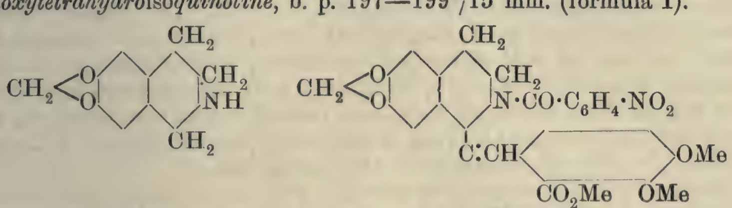
Cuspareine, $C_{16}H_{13}N(OMe)_2$, m. p. 55·5—56°, crystallises in long, colourless needles, forms salts with difficulty, but yields a crystalline methiodide, B,CH_3I,H_2O, m. p. 156° (decomp.), and this on treatment with silver chloride, followed by the addition of platinic chloride to the filtrate, yields the *methochloride platinichloride*, $(B,CH_3Cl)_2,PtCl_4,H_2O$, which is crystalline, sinters at 85°, and melts at 150° (decomp.). The free cuspareinemethylammonium base could not be isolated. On distillation with zinc dust, cuspareine furnishes quinoline. No

definite products could be obtained by the oxidation or reduction of the base.

Galipoidine, $C_{19}H_{15}O_4N$, m. p. 233°, is the name suggested for the new alkaloid described already (*loc. cit.*); it yields a *platinichloride*, $B_2,H_2PtCl_6,2\frac{1}{2}H_2O$, which crystallises in stout, yellow prisms and decomposes at 158°, and an *aurichloride*, $(B,HCl)_2,AuCl_3,1\frac{1}{2}H_2O$, m. p. 170° (decomp.), which crystallises in bright yellow needles.

T. A. H.

Synthesis of Oxyberberine. AMÉ PICTET and ALPHONSE GAMS (*Compt. rend.*, 1911, **152**, 1102—1105. Compare Perkin, Trans., 1889, **55**, 63; 1890, **57**, 992).—Piperonal condenses with opianic acid to form homopiperonylamine (Medinger, Abstr., 1906, i, 421). With formaldehyde in presence of hydrochloric acid, this furnishes *methylenedioxytetrahydro*iso*quinoline*, b. p. 197—199°/15 mm. (formula I).



(I.) (II.)

The o-*nitrobenzoyl* derivative of this substance (needles, m. p. 103—105°) is dissolved in sulphuric acid and treated with methyl opianate, when the *compound* (formula II) is obtained having m. p. 156—158°. On treatment with alcoholic potassium hydroxide, the latter undergoes hydrolysis with subsequent elimination of water between the imino- and carboxyl groups, and a substance is produced identical with Perkin's oxyberberine. The synthetic product is colourless, whereas the natural compound is coloured by impurities.

Oxyberberine yields a *chloro*-derivative when treated with phosphorus pentachloride, which on reduction forms a base resembling tetrahydroberberine, but not identical with it. W. O. W.

Corydalis Alkaloids. VII. (Protopine, Glaucine.) JOHANNES GADAMER (*Arch. Pharm.*, 1911, **249**, 224—233).—Previous investigations (Haars, Abstr., 1905, i, 462; Schmidt, 1909, ii, 85) have left it uncertain whether *Corydalis cava* contains protopine, although the widespread occurrence of this alkaloid in the order Papaveraceæ and its discovery by Makoshi in the tubers of *C. ambigua* (Abstr., 1908, i, 825) and *C. Vernyi* (*ibid.*, p. 908) made it probable that protopine was also present in *C. cava.* The author has therefore re-investigated the amorphous alkaloids obtained by Haars from the sub-aerial portion of *C. cava*, and finds that these consist of a mixture of phenolic and non-phenolic bases. The latter include protopine, glaucine, Haars' alkaloid, $C_{21}H_{23}O_7N$ (*loc. cit.*), a fourth *alkaloid*, giving a crystalline perchlorate, and a small quantity of alkaloid from which no crystalline derivatives could be obtained. The phenolic bases include bulbocapnine and at least two new *alkaloids*, which have as yet only been obtained crystalline as the *l*-acid

tartrates, of which one (base S) has $[\alpha]_D$ +20°, and the other (base R) has $[\alpha]_D$ +42°. These two bases are closely related to glaucine, and, like it, appear to belong to the bulbocapnine group. Full details are given of the method adopted in the separation of these alkaloids, and a list of the colour reactions of protopine and glaucine with various reagents.

The supposed new alkaloid obtained by Gaebel (Abstr., 1910, i, 501) from *Corydalis cava* is now shown to consist of *i*-corycavine with corycavidine in equal parts, but it is not quite certain whether a definite molecular compound of these two substances, having the properties noted by Gaebel, exists or whether his material is merely a mixture of the two. T. A. H.

Double Salts of Antimony Pentachloride with Various Alkaloid Hydrochlorides. TH. SV. THOMSEN (*K. Danske Selsk. Overs*, 1911, 41—55).—Ten grams of the alkaloid are dissolved in 200—300 c.c. of 90% alcohol, if necessary, with warming; to the solution are added 30—40 c.c. of 40% hydrochloric acid, and then the calculated quantity of antimony pentachloride, also dissolved in 40% hydrochloric acid (1 gram of antimony pentachloride in 4 c.c. of acid). The double salts separate after some time.

The antimony pentachloride does not have a chlorinating action on the alkaloid. The yield of double salt is 80—90%, except in the case of morphine, where it amounts to 50% only; in this latter case the mother liquors deposit an amorphous mass, which is probably a transformation product.

Quinine hydrochloride antimony pentachloride,

$$C_{20}H_{24}O_2N_2,2HCl,SbCl_5,$$

forms a sulphur-yellow, crystalline powder. *Quinidine hydrochloride antimony pentachloride*, $C_{20}H_{24}O_2N_2,2HCl,SbCl_5$, is obtained as yellow, three-sided prisms. *Cinchonine hydrochloride antimony pentachloride*, $C_{19}H_{22}ON_2,2HCl,SbCl_5,2H_2O$, forms pale yellow, prismatic columns.

Cinchonidine hydrochloride antimony pentachloride,

$$C_{19}H_{22}ON_2,2HCl,SbCl_5,H_2O,$$

forms pale yellow, rectangular plates. *Morphine hydrochloride antimony pentachloride*, $2C_{17}H_{19}O_3N,2HCl,SbCl_5,4H_2O$, is obtained as light brown, thin, irregular plates with serrated edges. *Codeine hydrochloride antimony pentachloride*, $2C_{18}H_{21}O_3N,2HCl,SbCl_5$, forms reddish-brown, irregular plates. *Strychnine hydrochloride antimony pentachloride*, $C_{21}H_{22}O_2N_2,HCl,SbCl_5$, is obtained as red, rhombic plates or short, rhombic prisms. *Cocaine hydrochloride antimony pentachloride*, $C_{17}H_{21}O_4N,HCl,SbCl_5$, forms colourless, thin, irregular plates with a satin glance. *Caffeine hydrochloride antimony pentachloride*, $C_8H_{10}O_2N_4,HCl,SbCl_5,H_2O$, forms yellow crystals of no definite shape. *Nicotine hydrochloride antimony pentachloride*,

$$2(C_{10}H_{14}N_2,2HCl),3SbCl_5,3H_2O,$$

is obtained as pale rose-red, columnar crystals. T. S. P.

Conversion of Glutamic Acid and of Pyrrolidonecarboxylic Acid into Proline. EMIL FISCHER and REGINALD BOEHNER (*Ber.*, 1911, 44, 1332—1337).—Ethyl pyrrolidonecarboxylate, the anhydride

of *d*-glutamic acid, when reduced by sodium and ethyl alcohol is converted into racemic proline.

Ethyl 5-*pyrrolidone*-2-*carboxylate*, prepared by esterification of *d*-glutamic acid with alcohol and anhydrous hydrogen chloride, and heating at 160—170° after removal of the alcohol, crystallises in needles or slender, colourless prisms, which soften at 49°, m. p. 54°. It has $[\alpha]_D^{16} - 2{\cdot}47°$, and contains no racemic compound, since on hydrolysis pure *d*-glutamic acid is formed. The corresponding *methyl* ester is a colourless oil, b. p. 180°/12 mm.

5-*Pyrrolidone*-2-*carboxylamide*, obtained by interaction of the ethyl ester with ammonia, has m. p. 165°, and is strongly lævorotatory.

E. F. A.

Pseudo-bases of the Pyridine Series. WILHELM KÖNIG (*J. pr. Chem.*, 1911, [ii], 83, 406—418).—Kaufmann and Strübin have recorded their opinion that the pseudo-ammonium bases of the quinoline, *iso*quinoline, and acridine series function as either carbinols or as unsaturated aldehydeamines (this vol., i, 321). This view, which which has been advanced and discussed by the author in 1907, is supported by the behaviour of the pseudo-bases of the pyridine series. The following example is an instance of the method by which such pseudo-bases are conveniently prepared. *m*-Chloroaniline and cyanogen bromide yield by Zincke's method (Abstr., 1904, i, 449, 921; compare also König, Abstr., 1904, i, 449, 816) the *pyridine dye*,

$C_6H_4Cl{\cdot}NH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH(OEt){\cdot}NH{\cdot}C_6H_4Cl,HBr$,

m. p. 165°, red needles with blue shimmer, which is converted by phenylhydrazine (2 mols.) into *α*-m-*chloroanilino*-*ε*-*phenylhydrazinopiperylene*, $C_{17}H_{16}N_3Cl$, m. p. 141°, yellow needles, and by warming with nitrobenzene yields m-*chlorophenylpyridinium bromide*, $C_{11}H_9NClBr$, m. p. 87—89°, colourless crystals, corresponding with which a *ferrichloride*, $C_{11}H_9NCl_2,FeCl_3$, m. p. 127—128°, sulphur-yellow leaflets, *ferribromide*, m. p. 120°, reddish-brown needles, *picrate*, m. p. 137—138°, citron-yellow needles, *dichromate*, decomp. 198°, orange leaflets, *platinichloride*, m. p. 191° (decomp.), and *aurichloride*, m. p. 182°, are described. By decomposing it with bromine, best in methyl alcohol (in glacial acetic acid, 3-*chloro*-2:4:6-*tribromoacetanilide*, m. p. 225°, is obtained as a by-product), the pyridine dye yields 3-*chloro*-2:4:6-*tribromophenylpyridinium perbromide*, $C_5H_5NBr_3{\cdot}C_6HClBr_3$, m. p. 171°, a solution of which in acetone is decomposed by ether with the formation of the corresponding *bromide*, $C_{11}H_6NClBr_4,2H_2O$ (from water), m. p. above 275° (*picrate*, m. p. 170°, *aurichloride*, m. p. 237°, *ferrichloride*, m. p. 154°, *platinichloride*, m. p. 233°). Finally, the *pseudo-base*, m. p. about 78° (decomp.), is obtained as a yellow precipitate, darkening in light, by treating a cold aqueous solution of the chlorotribromophenylpyridinium bromide with ammonium carbonate; it regenerates pyridinium salts by boiling with acids. When boiled with ethyl alcohol the pseudo-base yields a nearly colourless *ethyl alcoholate*, $C_{13}H_{13}O_2NClBr_3$, m. p. 122°; also with methyl alcohol a *methyl alcoholate*, $C_{12}H_{11}O_2NClBr_3$, m. p. 129°, is produced, which can also be obtained by crystallising the ethyl alcoholate from methyl alcohol. The formation of these compounds is explained by ascribing

the aldehydeamine formula, $C_6HClBr_3\cdot NH\cdot CH\colon CH\cdot CH\colon CH\cdot CHO$, to the pseudo-base; the alcoholates are then produced by the addition of the alcohols at the carbonyl group. C. S.

The Tautomerism of Isatin. F. Carlo Palazzo and G. Scelsi (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI, 243—244).—Isatin reacts with diazomethane or diazoethane at the ordinary temperature, forming *O*-ethers differing from those previously known, and assumed to be derived from a third modification of isatin, $C_6H_4<\begin{matrix}N\text{——}\\ |\\ C(OH)\end{matrix}>CO$. C. H. D.

Syntheses in the Indole Group. I. Alkylindoles. Bernardo Oddo (*Gazzetta*, 1911, 41, i, 221—234).—The preparation of homologues of indole has not previously been effected by the direct action of alkyl iodides, but the author finds that by using magnesium indolyl iodide these homologues can be readily obtained. The inorganic portion of the molecule is eliminated and the two organic radicles unite, giving the indole substituted in the 3-position:

$$C_8H_6N\cdot MgX + R\cdot X = MgX_2 + C_6H_4<\begin{matrix}CR\\ NH\end{matrix}>CH.$$

In some cases, owing to differences in the experimental conditions difficult to define, the alkyl enters in the 1-position, and in these cases traces of the 1:3-dialkyl derivative are also formed. The elimination of the inorganic portion of the magnesium indolyl iodide is facilitated by the presence of a small proportion of calcined potassium chloride. Since it is observed that when the halogen is the same in the two molecules the double decomposition occurs with difficulty, but that chloro-derivatives react readily with magnesium alkyl iodides, the action of the potassium chloride may be regarded as catalytic in nature: $RI + KCl = KI + RCl$. In this way the author has prepared the following indole derivatives:

(1) Scatole (3-methylindole), which is accompanied by a small proportion of a non-basic compound forming microscopic, pale yellow, bipyramidal crystals, m. p. 197—200°. (2) 1-Methylindole, which is formed along with traces of a product forming yellow crystals, m. p. 197—200°; and (3) 3-ethylindole.

Magnesium indolyl iodide forms an additive compound with pyridine, $C_{11}H_{11}N_3MgI$, as a flocculent, white precipitate; with water this compound yields indole, pyridine and magnesium iodide and hydroxide.

Addition of saturated mercurous nitrate solution to an alcoholic solution of scatole (or indole) results in the formation of a yellow (or greyish-green) precipitate insoluble in water. With mercuric nitrate, under the same conditions, scatole gives a pale yellow and indole a grey precipitate. With mercuric chloride, scatole or indole or 2-methylindole gives a white precipitate. T. H. P.

Syntheses in the Indole Group. II. Alkylindolyl Ketones and Indole Acids. Bernardo Oddo and Luigi Sessa (*Gazzetta*, 1911, 41, i, 234—248. Compare preceding abstract).—The action of

acyl chlorides on magnesium indolyl iodide in presence of ether at the ordinary temperature gives rise to 3-acylindoles (indolyl alkyl ketones), $C_6H_4<\genfrac{}{}{0pt}{}{C\cdot COR}{NH\text{——}}>CH$, which are accompanied by small proportions of 1 : 3-diketones, $C_6H_4<\genfrac{}{}{0pt}{}{C(COR)}{N(COR)}>CH$.

Thus, acetyl chloride and magnesium indolyl iodide yield 3-acetylindole (3-indolyl methyl ketone) (compare von Baeyer, Abstr., 1879, 36, 937), the *phenylhydrazone* of which,

$$NH<\genfrac{}{}{0pt}{}{C_6H_4}{-CH}>C\cdot CMe\!:\!N_2HPh,$$

forms pale yellow, acicular crystals, m. p. 118°. 1 : 3-Diacetylindole (compare von Baeyer, *loc. cit.*) is formed in small amount with the 3-acetyl compound.

3-*Indolyl ethyl ketone* (3-*propionylindole*), $C_6H_4<\genfrac{}{}{0pt}{}{C(COEt)}{NH\text{———}}>CH$, prepared from propionyl chloride and magnesium indolyl iodide, forms crystals, m. p. 157—158°, and, on fusion with potassium hydroxide, yields indole-3-carboxylic acid. Its *oxime*, $C_{11}H_{12}ON_2$, forms white crystals, m. p. 120—122°, and its *phenylhydrazone*, $C_{17}H_{17}N_3$, red crystals, m. p. 109—110°. It is accompanied by 1 : 3-*dipropionylindole*,

$$C_6H_4<\genfrac{}{}{0pt}{}{C(COEt)}{N(COEt)}>CH,$$

m. p. 128—130°, which is converted into 3-propionylindole on boiling with 50% potassium hydroxide solution.

3-*Indolyl propyl ketone* (3-*butyrylindole*), $NH<\genfrac{}{}{0pt}{}{C_6H_4}{-CH}>C\cdot COPr^{a}$, prepared from butyryl chloride and magnesium indolyl iodide, forms white crystals, m. p. 169°, and yields a crystalline phenylhydrazone, m. p. 107°.

3-*Indolyl phenyl ketone* (3-*benzoylindole*), $NH<\genfrac{}{}{0pt}{}{C_6H_4}{-CH}>CBz$, prepared from benzoyl chloride and magnesium indolyl iodide, forms red crystals, m. p. 170°, and is probably mixed with a little 1 : 3-dibenzoylindole, since, on boiling with 50% potassium hydroxide solution and a small quantity of alcohol, the m. p. rises to 227°. The *phenylhydrazone*, $C_{21}H_{17}N_3$, forms yellow crystals, m. p. 192—194°, and the *silver* derivative is a precipitate soluble in excess of ammonia.

The action of carbon dioxide on magnesium indolyl iodide in anhydrous ethereal solution, yields *indole*-1-*carboxylic acid*,

$$CH<\genfrac{}{}{0pt}{}{C_6H_4}{CH-}>N\cdot CO_2H,$$

m. p. 108°, which is decomposed by boiling water into indole and carbon dioxide and gives a white precipitate with barium chloride or lead acetate solution. The formation of the acid proceeds thus:

$$CH<\genfrac{}{}{0pt}{}{C_6H_4}{CH-}>N\cdot MgI + O\!:\!C\!:\!O = CH<\genfrac{}{}{0pt}{}{C_6H_4}{CH-}>N\cdot CO\cdot O\cdot MgI \longrightarrow$$

$$CH<\genfrac{}{}{0pt}{}{C_6H_4}{CH-}>N\cdot CO_2H.$$

Ethyl indole-2-carboxylate, $C_6H_4<\overset{CH}{\underset{NH}{}}>C\cdot CO_2Et$, prepared by the interaction of ethyl chlorocarbonate and magnesium indolyl iodide, forms white crystals, m. p. 107°. T. H. P.

Transpositions with the Organo-magnesium Compounds. I. BERNARDO ODDO (*Gazzetta*, 1911, 41, i, 255—272; and, in part, *7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI., 226—231).—In order to ascertain whether it is possible to obtain organo-magnesium compounds in which the MgX-radicle shall be attached first and with certainty to a nitrogen atom, the author has made use of carbazole, which is analogous in constitution to pyrrole and indole (compare preceding abstracts and this vol., i, 496), and of diphenylamine; in both of these compounds the iminic nitrogen is united to two quaternary carbon atoms, and in carbazole, in addition, two of the carbon atoms adjacent to these quaternary carbon atoms are devoid of hydrogen.

It is found that carbazole readily gives the compound

$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}>N\cdot MgI,OEt_2,$$

and a similar result is obtained with diphenylamine.

The iodomagnesium derivative of carbazole is readily acted on by acyl chlorides, but not by alkyl iodides, and the latter act the less readily with organo-magnesium indole compounds. The action of an acid chloride seems to be favoured by the presence of the double linking between oxygen and carbon, an additive product being formed first:

$$R{:}N\cdot MgI + O{:}CR'Cl = R{:}N\cdot CR'Cl\cdot O\cdot MgI = MgICl + R{:}N\cdot CO\cdot R'.$$

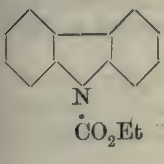
It was shown by Oddo and Mameli (Abstr., 1902, i, 33) that Kolbe's reaction between sodium phenoxides and carbon dioxide for the formation of the aromatic hydroxy-acids takes place, in some cases, in presence of neutral solvents. The author has now investigated the action of carbon dioxide on the iodomagnesium derivatives of various phenols, which undergo conversion into the corresponding hydroxy-acids. With the phenol and the resorcinol derivatives, this change occurs only in absence of solvent, and at a high temperature, the acid in latter case having the constitution: $CO_2H:(OH)_2 = 1:2:4$. With derivatives of the following phenols, the reaction proceeds in presence of solvent (benzene or toluene): β-naphthol, which gives β-naphthol-α-carboxylic acid; phloroglucinol, giving phloroglucinolcarboxylic acid; thymol, giving *o*-thymotic acid [$CH_3:CO_2H:OH:C_3H_7 = 1:2:3:4$]; *o*-cresol, giving *o*-cresotic acid; and carvacrol, giving carvacrotic acid [$CH_3:OH:C_3H_7:CO_2H = 1:2:4:6$].

The *compound*, $C_{12}H_8N\cdot MgI,OEt_2$, is obtained as a white, amorphous powder, and, on treatment with carbon dioxide in presence of ether, toluene or cymene, it is converted into the unstable *acid*,

$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}>N\cdot CO_2H.$$

If, however, the carbon dioxide acts at a high temperature (265—270°) and in absence of solvent, Ciamician and Silber's carbazole-carboxylic acid, $CO_2H\cdot C_6H_3<\begin{matrix}NH\\|\\C_6H_4\end{matrix}$ (Abstr., 1882, 42, 1103), is obtained.

Diphenyleneurethane [*Ethyl carbazole-9-carboxylate*] (annexed formula), prepared by the action of ethyl chlorocarbonate on the iodomagnesium derivative of carbazole, crystallises in needles, m. p. 77·5°, and has the normal molecular weight in freezing benzene. On heating with alcoholic potassium hydroxide or with ammonia in a sealed tube, it is decomposed into carbazole, alcohol, and carbon dioxide.



Acetylcarbazole, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>NAc$, and the corresponding benzoylcarbazole may be readily prepared by the action of acetyl and benzoyl chlorides on the iodomagnesium compound.

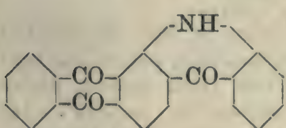
The *iodomagnesium* derivative of *diphenylamine*, $NPh_2{\cdot}MgI$, forms a greyish-brown oil, and is converted by carbon dioxide into the *acid*, $C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$, which forms silvery-white scales, m. p. 152°; the *silver* and *barium* salts of this acid were prepared. With ethyl chlorocarbonate the iodomagnesium derivative gives diphenylurethane, $CO_2Et{\cdot}NPh_2$. T. H. P.

Anthraquinone Series. IV. Anthraquinone-1 : 2-acridone and Anthraquinonediacridone. FRITZ ULLMANN and PAUL OCHSNER (*Annalen*, 1911, **381**, 1—11. Compare Abstr., 1910, i, 270, 696; this vol., i, 136; following abstract).—A 95% yield of 1-chloroanthraquinone can be obtained by dropping a solution of sodium chlorate into a well-stirred boiling solution of potassium anthraquinone-1-sulphonate and concentrated hydrochloric acid. It crystallises from alcohol in yellow needles, m. p. 162°. The method appears to be a general one for replacing sulphonic acid groups in the anthraquinone series by chlorine (compare D.R.-P. 77179 and 205195). It affords a convenient method for identifying the various sulphonic acids, as the corresponding chlorine derivatives have definite melting points.

Anthraquinone-1-anilino-o-carboxylic acid,

$$C_6H_4{:}(CO)_2{:}C_6H_3{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H,$$

may be obtained by the catalytic action of copper on *o*-chlorobenzoic acid and 1-aminoanthraquinone, or, better, on anthranilic acid and 1-chloroanthraquinone. In the latter case, amyl alcohol is used as solvent, together with potassium acetate and finely-divided copper at a temperature of 150—160°. It crystallises from glacial acetic acid in Bordeaux-red plates, m. p. 282°. Its solution in pyridine has a red colour, but turns violet on the addition of a little water. The *alkali* salts are sparingly soluble in water, and have a bluish-violet colour. The anhydride, *anthraquinone-1 : 2-acridone* (annexed formula), is formed by the action of concentrated sulphuric acid on the acid at 100—110°, or in a purer form by transforming the acid into its chloride and boiling this for some minutes with nitrobenzene. It forms violet crystals with a coppery lustre, is readily reduced by alkali and hyposulphite, and dyes cotton a reddish-blue. The *bromo*-derivative, $C_{21}H_{10}O_3NBr$, obtained by the

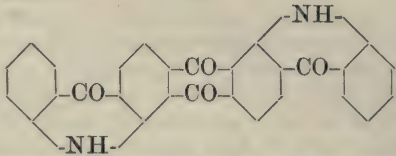


action of bromine on a nitrobenzene solution of the acridone, crystallises in red needles, m. p. 339° (corr.).

1 : 5-Dichloroanthraquinone and anthranilic acid with nitrobenzene, potassium acetate, copper acetate, and a little copper powder at 200° yield *anthraquinone*-1 : 5-*dianilinodi*-o-*carboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot NH\cdot C_6H_4\colon(CO)_2\colon C_6H_4\cdot NH\cdot C_6H_4\cdot CO_2H;$$

it crystallises from glacial acetic acid, in which it is sparingly soluble, in reddish-violet needles, m. p. 349° (corr.). *Anthraquinone*-2 : 1 : 6 : 5-*diacridone* :



crystallises from nitrobenzene in bluish-violet needles, m. p. 360°, and it dyes cotton the same colour. Its solubility in boiling nitrobenzene is only 1 in 1000. J. J .S.

Anthraquinone Series. V. Dichloroanthraquinones. FRITZ ULLMANN and GERHARD BILLIG (*Annalen*, 1911, **381**, 11—28).—1 : 2-, 2 : 3-, and 1 : 4-Dichloroanthraquinones have been synthesised from the corresponding dichlorophthalic acids. The product described by Kircher (Abstr., 1887, 831) as 1 : 2-dichloroanthraquinone is shown to be the 2 : 3-compound. The product described by Hammerschlag (Abstr., 1886, 717) has the same m. p. as the 1 : 2-dichloroanthraquinone, namely, 208°, but a mixture of the two melts at 175—180°.

The 1 : 4-derivative is reactive, and the two chlorine atoms can be replaced by phenoxy-, anilino-, and similar groups ; with anthranilic acid, however, only one chlorine atom is replaced.

3 : 6-*Dichloro-2-benzoylbenzoic acid*, $CO_2H\cdot C_6H_2Cl_2\cdot COPh$, crystallises from benzene in glistening, colourless prisms, m. p. 168·5° (corr.). 1 : 4-Dichloroanthraquinone, $C_{14}H_6O_2Cl_2$, is obtained when the finely divided acid (1 part) is added gradually to concentrated sulphuric acid (20 parts) heated at 160°, cooled to 70—80°, and ice added. It crystallises from glacial acetic acid in orange-yellow needles, m. p. 187·5° (corr.), and reacts with sodium phenoxide in the presence of finely divided copper, yielding 1 : 4-diphenoxyanthraquinone, $C_{26}H_{16}O_4$, which crystallises from alcohol in yellow needles, m. p. 165°. The solution in concentrated sulphuric acid has a bluish-violet colour (compare Walsh and Weizmann, Trans., 1910, **97**, 685).

1 : 4-*Di*-p-*tolylsulphonamidoanthraquinone*,

$$C_6H_4(CO)_2\cdot C_6H_2(NH\cdot SO_2\cdot C_7H_7)_2,$$

prepared by boiling for two hours a solution of the chlorinated quinone in nitrobenzene with *p*-toluenesulphonamide, potassium carbonate, and a little copper acetate, crystallises from boiling acetic acid in large, glistening, reddish-brown needles, m. p. 225°. Its solubility in boiling glacial acetic acid is 1 in 200. 1 : 4-Diaminoanthraquinone (Noelting and Wortmann, Abstr., 1906, i, 291) gives a violet-blue solution in glacial acetic acid, and reddish-violet solutions in benzene or pyridine. 1 : 4-*Dianilinoanthraquinone*, $C_{26}H_{18}O_2N_2$,

crystallises from glacial acetic acid in glistening, blue plates with a brown lustre; it has m. p. 217°, and is coloured greenish-blue by concentrated sulphuric acid.

1 : 4-*Di-a-aminoanthraquinoylanthraquinone*,

$$C_6H_4{:}(CO)_2{:}C_6H_2(NH{\cdot}C_{14}H_7O_2)_2,$$

obtained by condensing the chlorinated quinone with 1-aminoanthraquinone, is insoluble in practically all organic solvents, and, after purifying by extracting successively with toluene, aniline, alcohol, and dilute hydrochloric acid, forms glistening, violet needles, which are not fused at 410°.

4-*Chloro*-1-o-*carboxyanilinoanthraquinone*,

$$C_6H_4{:}(CO)_2{:}C_6H_2Cl{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H,$$

obtained by condensing 1 : 4-dichloroanthraquinone and anthranilic acid in hot amyl-alcoholic solution in the presence of potassium acetate and copper acetate for fifteen hours, crystallises from glacial acetic acid (1 in 200) in felted, Bordeaux-red needles, m. p. 262—263° (corr.), and gives a dark green coloration with concentrated sulphuric acid. The acid chloride in the presence of boiling nitrobenzene yields 4-*chloroanthraquinone*-2 : 1-*acridone* $C_6H_4{:}(CO)_2{:}C_6HCl{<}{}^{NH}_{CO}{>}C_6H_4$, in the form of glistening, violet needles, m. p. 267° (corr.), which dye cotton reddish-violet.

4-p-*Toluenesulphonamidoanthraquinone*-2 : 1-*acridone*,

$$C_6H_4{:}(CO)_2{:}C_6H(NH{\cdot}SO_2{\cdot}C_7H_7){<}{}^{NH}_{CO}{>}C_6H_4,$$

crystallises from nitrobenzene in small, bluish-black needles, m. p. 295°. Its solubility in boiling glacial acetic acid is 1 in 3000. 4-*Aminoanthraquinone*-2 : 1-*acridone*, $C_{21}H_{12}O_3N_2$, obtained by hydrolysing the toluenesulphonamido-derivative with sulphuric acid, crystallises from nitrobenzene in dark blue needles, which are not molten at 410°, and dyes cotton blue.

4-p-*Toluidinoanthraquinone*-2 : 1-*acridone*, $C_{28}H_{18}O_3N_2$, crystallises from nitrobenzene in glistening, bluish-green needles, m. p. 300°.

4-a-*Aminoanthraquinoylanthraquinone*-2 : 1-*acridone*,

$$C_6H_4{:}(CO)_2{:}C_6H(NH{\cdot}C_{14}H_7O_2){<}{}^{NH}_{CO}{>}C_6H_4,$$

forms felted, violet needles, insoluble in organic solvents, and dyes cotton a bluish-green.

3 : 4- or 5 : 6-Dichlorobenzoylbenzoic acid has m. p. 216°. 1 : 2-*Dichloroanthraquinone* crystallises from glacial acetic acid in golden-yellow needles, m. p. 208°.

4 : 5-*Dichlorobenzoylbenzoic acid* crystallises from benzene in glistening, colourless needles, m. p. 209°, and with concentrated sulphuric acid yields 2 : 3-*dichloroanthraquinone*, which crystallises from glacial acetic acid in long, pale yellow needles, m. p. 267° (corr.).

J. J. S.

Preparation of 5-Methyl*iso*oxazole from the Acetals of Tetrolaldehyde. LUDWIG CLAISEN (*Ber.*, 1911, 44, 1161—1169).—Starting from crotonaldehyde, the author has synthesised 5-methyl*iso*-

oxazole, and finds that it is identical in all respects with the compound previously described (Abstr., 1909, i, 185).

αβ-Dibromobutaldehyde has b. p. 75—82°/14 mm., and is converted by sodium acetate into *α*(?)-bromocrotonaldehyde (compare Viguier, Abstr., 1910, i, 461). When methylated by means of methyl-orthoformate in methyl-alcoholic solution, this gives *β(?)-bromo-αα-dimethoxy-Δ^β-butylene*, $C_3H_4Br\cdot CH(OMe)_2$, a colourless liquid, b. p. 175°, under ordinary pressure, or 59°/10 mm., D^{15} 1·357, having an odour of camomile. The diethoxy-compound may be prepared in a similar manner.

αα-Dimethoxybutinene, $CMe\vdots C\cdot CH(OMe)_2$, prepared by heating the preceding bromodimethoxy-derivative with methyl-alcoholic potassium hydroxide, is a colourless liquid with a penetrating odour, b. p. 144—145°, D^{15} 0·954. It is converted by continued heating with sodium methoxide in methyl-alcoholic solution into an oil, b. p. 160—166°, consisting probably of *ααγ-trimethoxy-Δ^β-butylene*,

$$OMe\cdot CMe\colon CH\cdot CH(OMe)_2.$$

Tetrolaldehyde, $CMe\vdots C\cdot CHO$, obtained in small yield by hydrolysing dimethoxybutinene with mineral acids, is a colourless liquid, with an intolerably sharp odour, resembling acraldehyde; it is decomposed by cold aqueous sodium hydroxide into allylene and sodium formate. The *oxime*, C_4H_5ON, obtained together with 5-methyl*iso*oxazole by shaking dimethoxybutinene with aqueous hydroxylamine hydrochloride and a small quantity of hydrochloric acid, crystallises in large needles, m. p. 103°. On treatment with excess of sodium hydroxide or of alcoholic sodium ethoxide, it is transformed with explosive violence into cyanoacetone. With minute quantities of sodium hydroxide, it yields 5-methyl*iso*oxazole. The transformation into the latter compound is, however, best effected with aqueous sodium carbonate.

F. B.

Esterification of the *iso*Oxazolones with Diazomethane. E. Oliveri-Mandalà and A. Coppola (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 244—249).—To ascertain if the *iso*oxazolones can behave tautomerically, like their analogues the pyrazolones, the authors have investigated the esters obtainable from them by the action of diazomethane.

γ-Methyl*iso*oxazolone yields an *N*-methyl derivative, m. p. 74°, identical with that prepared by Uhlenhuth (Abstr., 1897, i, 444), and a *C*-methyl *derivative*, $C_9H_{10}O_3N_2$, m. p. 163—164°, which may be separated from the former by reason of its insolubility in light petroleum; it crystallises in very small needles. Both substances are obtained in the form of a condensation product of one molecule of the ester with one molecule of the methyl*iso*oxazolone, and Uhlenhuth observed a similar behaviour in the case of the salts.

γ-Phenyl*iso*oxazolone gives an *N*-methyl derivative, m. p. 77—78°, identical with that of Uhlenhuth (*loc. cit.*), and also an O-*ester*, $\begin{matrix} CPh{=\!=\!=}N \\ | \\ CH{=}C(OMe) \end{matrix}\!\!>\!O$, m. p. 70°, which crystallises in silky needles and contains one methoxyl group.

R. V. S.

[Preparation of Methyl-2 : 4-diaminoanisole.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 230630).—*Methyl*-2 : 4-*diaminoanisole*, a colourless oil, b. p. 180°/15 mm., and very sparingly soluble in water, is prepared by the action of methyl sulphate on an aqueous solution of 2 : 4-diaminoanisole at 40—50°.

F. M. G. M.

[Preparation of Dichlorodinitrobenzidine.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 229029).—2 : 2′-*Dichloro*-5 : 5′-*dinitrobenzidine*, a yellow powder, m. p. 255°, is obtained by the nitration and subsequent hydrolysis of 2 : 2′-dichlorodiacetylbenzidine; when tetrazotised and combined with 2 mols. of β-naphthol, it yields 2 : 2′-*dichloro*-5 : 5′-*dinitrodiphenylbisazo-β-naphthol*, a red substance which (being soluble in oils) is suitable for employment as a pigment.

F. M. G. M.

***holo*- and *meri*-Quinonoid Salts of Benzidine.** JEAN PICCARD (*Ber.*, 1911, **44**, 959—960. Compare this vol., i, 323).—Polemical. Madelung claims to have proved the existence of strongly-coloured *holo*-quinonoid imonium salts of benzidine. When a *meri*-quinonoid salt is precipitated and a further amount of bromine added to the filtered salt, a *meri*-quinonoid salt of a brominated benzidine and not a *holo*-quinonoid salt is formed. Benzidine with less than two atoms of halogen yields bluish-violet, blue or green *meri*-quinonoid salts, whereas the *holo*-quinonoid imonium salt with two atoms of halogen is only yellow in colour.

E. F. A.

Resolution of Asymmetric Diammonium Compounds into Optical Antipodes. EMIL FRÖHLICH (*Ber.*, 1911, **44**, 1057—1070).—The author has prepared substances of the type $Y(NR'R'')_2$, where $Y = CH_2$, C_2H_4, or C_3H_6, and R′ and R″ are various alkyl or aryl groups (Abstr., 1907, i, 346). By the addition of alkyl or aryl halogenides, R‴X, asymmetric diammonium compounds should be formed. This happens, however, only when Y is C_3H_6; thus Wedekind has obtained two series of isomeric trimethylenebisphenylmethylethylammonium derivatives, which, however, he was unable to resolve into optically active components (Abstr., 1910, i, 834). The author attributes the failure to the presence of impurities, and has therefore prepared other series of the di-tertiary bases in a pure state. First he obtained NN′-*dimethyl*-NN′-*diethylbenzidine*, $NMeEt{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NMeEt$, m. p. 110°, by oxidising methylethylaniline with concentrated sulphuric acid, but found that it formed only a *mono-allyloiodide*, $NMeEt{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NMeEt(C_3H_5)I$, m. p. 154—155° (decomp.), and *monobenzylobromide*,

$$NMeEt{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NMeEtBr{\cdot}CH_2Ph,$$

m. p. 146—147° (decomp.). Better results, however, have been obtained with derivatives of pp′-diaminodiphenylmethane. NN′-*Dimethyl*-NN′-*diethyl*-pp′-*diaminodiphenylmethane*, $CH_2(C_6H_4{\cdot}NMeEt)_2$, m. p. 40°, b. p. 282°/40 mm., obtained by boiling methylethylaniline with concentrated hydrochloric acid and 34% formaldehyde for three to four hours, forms additive compounds with 2 mols.

of allyl iodide or of benzyl bromide. Theoretically two isomerides belonging to the *para-* and the *meso*-series respectively should be produced in each case, but experience shows that the *as*-diammonium salts are individual and belong to the *para*-series (since the allyl derivative has been resolved into its active components). Thus p-*methylenebisphenylenebisallylmethylethylammonium iodide*,

$$CH_2(C_6H_4\cdot NMeEtI\cdot C_3H_5)_2,$$

m. p. 174° (decomp.), obtained from *NN'*-dimethyl-*NN'*-diethyl-*pp'*-diaminodiphenylmethane and allyl iodide (2 mol.) in alcohol, is resolved by silver *d*-camphorsulphonate in alcohol-acetone solution. The less soluble *dicamphorsulphonate*, as first precipitated, has m. p. 159—160° and $[M]_D$ +89·32°. It is purified by solution in alcohol and precipitation by ether. After twenty-four repetitions of this operation a fraction is obtained having m. p. 159—160° and $[M]_D$ +34·06°, from which the value $[M]_D$ −69·34° is calculated for the active diammonium ion. From the active dicamphorsulphonate the active *di-iodide* is obtained by addition of potassium iodide; it has m. p. 174° and $[M]_D$ −68·66° in alcoholic solution. The alcohol-acetone mother liquor, from which the active dicamphorsulphonate has been precipitated, is concentrated and treated with ether, the oil obtained is dissolved in warm water and treated with potassium iodide, whereby d-p-*methylenebisphenylenebisallylmethylethylammonium iodide*, m. p. 174°, is obtained; the maximal value of $[M]_D$ is +29·93°. p-*Methylenebisphenylenebisallylmethylethylammonium bromide*, m. p. 205° (decomp.), can also be resolved by silver *d*-camphorsulphonate, but in consequence of the slight difference in the solubilities of the two dicamphor sulphonates the fractionation has not been continued.

An alcoholic solution of *NN'*-dimethyl-*NN'*-diethyl-*pp'*-diaminodiphenylmethane reacts with benzyl iodide (2 mols.) to form p-*methylenebisphenylenebisbenzylmethylethylammonium iodide*, m. p. 129—130° (decomp.), and with benzyl bromide (2 mols.) to form the corresponding *dibromide*, m. p. 145° (decomp.); the latter yields with silver *d*-camphorsulphonate a *dicamphorsulphonate*, $C_{53}H_{70}O_8N_2S_2$, m. p. 130—140°, which has $[M]_D$ +97·07°, and therefore shows practically no indication of being resolved ($[M]_D$ = +103·4° for two *d*-camphorsulphonic ions).

NN-*Dimethyl*-NN'-*dipropyl*-pp'-*diaminodiphenylmethane*,

$$CH_2(C_6H_4\cdot NMePr^a)_2,$$

b. p. 295—297°/40 mm., obtained from methylpropylaniline, hydrochloric acid, and formaldehyde, combines with alcoholic allyl iodide to form p-*methylenebisphenylenebisallylmethylpropylammonium iodide*, $C_{27}H_{38}N_2I_2$, m. p. 140° (decomp.), and with allyl bromide to form the corresponding *dibromide*, m. p. 135° (decomp.); the *di*-d-*camphorsulphonate*, $C_{47}H_{70}O_8N_2S_2$, has m. p. 130° (decomp.) and $[M]_D$ +102·3°, and cannot be resolved into its two components. C. S.

The Oxidation and Auto-reduction of Hydrazines. FREDERICK D. CHATTAWAY (*Chem. News*, 1911, **103**, 217—218. Compare Trans., 1911, **99**, 404).—Phenylhydrazine readily absorbs oxygen with development of heat, gives off nitrogen, and forms benzene. The reaction is found to be general for all aromatic

hydrazines: $2RHN-NH_2+O_2=2RH+2N_2+2H_2O$. The author supposes that a hydrogen atom of the $-NH_2$-group is first attacked with production of a hydroxy-hydrazine, which, being unstable, undergoes a disruption analogous to the typical diazonium decomposition. Potassium hydroxide, and to a less extent sodium hydroxide, very much accelerates the rate of oxidation; indeed, on exposing to the air a solution of phenylhydrazine in alcoholic potash the temperature rises, and nitrogen is rapidly given off with vigorous effervescence. Potassium chromate in alkaline solution acts in the same way; the reaction is quantitative, so that the evolved nitrogen can be used as a measure of the amount of hydrazine present. The reaction further affords the most satisfactory method known of replacing an amino-group by hydrogen; the amino-group is converted through the diazonium salt into the hydrazine group, which is then oxidised as above. E. J. R.

Experiments on the Preparation of Derivatives of Hydroxyhydrazines. HEINRICH WIELAND and HANS FRESSEL (*Ber.*, 1911, **44**, 898—904).—Attempts have been made to synthesise derivatives of hydroxyhydrazine by the action of Grignard reagents on nitrosoamines, according to the scheme:

$$NR_2\cdot NO+R'MgX \longrightarrow NR_2\cdot NR'\cdot OH,$$

but so far without success.

Diethylnitrosoamine reacts with magnesium ethyl iodide, yielding ethane and a liquid consisting mainly of acetaldehydediethylhydrazone. The latter compound is produced from the initial additive product, $NEt_2\cdot NEt\cdot O\cdot MgI$ by the loss of $MgI\cdot OH$, which then reacts with a second molecule of magnesium ethyl iodide to form ethane. For the purpose of comparison, *acetaldehydediethylhydrazone*,

$$CHMe{:}N\cdot NEt_2,$$

was prepared by the interaction of acetaldehyde and diethylhydrazine in aqueous solution. It has b. p. 123—126°, and is readily decomposed by dilute mineral acids into its components.

Dimethylnitrosoamine, on treatment with magnesium methyl iodide, yields methane, the reaction apparently proceeding in a similar manner to that already described in the case of diethylnitrosoamine.

When diphenylnitrosoamine is treated with magnesium ethyl iodide, ethane and acetaldehydediphenylhydrazone are produced.

The interaction of diethylnitrosoamine and magnesium phenyl bromide leads to the formation of *α-phenyl-β(α)-phenylethyl-β-ethylhydrazine*, $NHPh\cdot NEt\cdot CHMePh$, and *α-phenyl-ββ-diethylhydrazine*, $NEt_2\cdot NHPh$. The latter compound is a light yellow, viscid oil, b. p. 110—112°/14 mm., having a geranium-like odour, and forms a yellow, oily *nitroso*-compound, a crystalline *hydrochloride*, and a yellow *picrate*, m. p. 131°. When reduced with zinc dust and glacial acetic acid it yields aniline and diethylamine.

α-Phenyl-β(α)-phenylethyl-β-ethylhydrazine is a greenish-yellow, viscid oil, b. p. 177°/10 mm. It forms an oily *nitroso*-compound, which decomposes when kept, yielding benzenediazonium chloride; its salts were all obtained in the form of oils. When reduced with zinc

and glacial acetic acid, it yields aniline and *a-phenylethylethylamine*, NHEt·CHMePh. The last-mentioned compound, which, for the purpose of comparison, was also prepared by the interaction of a-phenylethylamine and ethyl sulphate, has b. p. 125—127°/94 mm., and forms a *hydrochloride*, crystallising in slender needles, m. p. 196—197°; the *nitrosoamine* is a yellow oil.

The formation of phenyldiethylhydrazine by the action of magnesium phenyl bromide on diethylnitrosoamine is due to the reduction of the initial additive product, NEt_2·NPh·O·MgBr, whilst the formation of a-phenyl-β(a)-phenylethyl-β-ethylhydrazine is referred by the authors to the intermediate production of a cyclic hydrazi-compound:

$$\begin{matrix} NEt \\ | \\ NPh \end{matrix} > CH \cdot Me.$$

Under the influence of a second molecule of magnesium phenyl bromide, the ring of the latter compound is opened with the formation of phenyl-a-phenylethylethylhydrazine, the addition of C_6H_5 and H taking place at the position indicated by the dotted line.

F. B.

Syntheses in the Pyrrole Group. III. Dipyrroyl and its Derivatives. BERNARDO ODDO (*Gazzetta*, 1911, 41, i, 248—255).—Since ketonic compounds are readily formed from magnesium pyrryl iodide and acyl chlorides corresponding with monocarboxylic acids (compare Abstr., 1910, i, 426), the author has investigated the reaction in the case of the chlorides of dibasic acids, the α-, β-, γ-, etc., diketones with pyrrole nuclei, which should be formed, being unknown. It is found that these compounds are actually formed, the reaction being apparently of general applicability, although Lemaire (*Rec. trav. chim.*, 1910, 39) was unable to obtain either an alcoholic or a ketonic compound by the action of malonyl chloride on the ordinary Grignard compounds; further, it has not been found possible to prepare aromatic ortho-diketones or the chlorides of a-keto-acids from oxalyl chloride by means of Friedel and Craft's reaction, this chloride being decomposed quantitatively by aluminium chloride into carbon monoxide and carbonyl chloride.

[With GEROLAMO ANDÒ.]—*Dipyrroyl* (*dipyrroyl-a:a-diketone*),

$$\begin{matrix} CH\cdot CH \\ \| \\ CH\cdot NH \end{matrix} > C\cdot CO\cdot CO\cdot C < \begin{matrix} CH\cdot CH \\ \| \\ NH\cdot CH \end{matrix},$$

pale yellow crystals, m. p. 199·5—200°, is prepared from oxalyl chloride and magnesium pyrryl iodide, the reaction proceeding violently unless cooling with a freezing mixture and dilution with ether are resorted to. It exhibits normal cryoscopic behaviour in acetic acid and forms a *diphenylosazone*, C_4NH_4·C(N_2HPh)·C(N_2HPh)·C_4NH_4, yellowish-red needles, m. p. 146°, which, when heated with alcohol and ferric chloride, yields a reddish-brown compound, probably

$$\begin{matrix} C_4NH_4\cdot C\!:\!N\cdot NPh \\ | \qquad\quad | \\ C_4NH_4\cdot C\!:\!N\cdot NPh \end{matrix}.$$

It forms also a dioxime, to be studied later in its relation to dibenzoyl, which gives three stereoisomeric dioximes. It does not give Bamberger's

colour reaction for 1 : 2-diketones (compare Abstr., 1885, 807), but with *o*-phenylenediamine it yields *dipyrrylquinoxaline*,

$$C_6H_4<\begin{matrix}N:C\cdot C_4NH_4 \\ N:C\cdot C_4NH_4\end{matrix},$$

which forms chrome-yellow, twinned crystals, m. p. 158°, and gives the general reactions of the quinoxalines.

Dipyrroyl yields a *silver* derivative, $C_4NH_3Ag\cdot CO\cdot CO\cdot C_4NH_3Ag$, as a yellow precipitate, and, on oxidation with permanganate, gives ketopyrrolic acid (compare Holleman, Abstr., 1904, i, 474).

T. H. P.

Preparation of Indigotin from Indole. GESELLSCHAFT FÜR TEERVERWERTUNG (D.R.-P. 230542).—The partial conversion of indole into indigotin by oxidation with ozonised air has previously been recorded; it is now found that the reaction is complete, and a pure product obtained if the indole is converted into β-indolecarboxylic acid, purified, dissolved in a mixture of acetone and sodium hydroxide, and treated with ozonised air until the separation of indigotin is complete.

F. M. G. M.

Theory of Indigo Dyeing. ARTHUR BINZ and K. MANDOWSKY (*Ber.*, 1911, **44**, 1225—1229).—It is well known that the dyes of the indigo group readily form additive compounds with sodium hydroxide; indigotin itself reacts slowly on account of its insolubility, but readily forms an additive compound with sodium ethoxide. The addition does not occur, however, when the indigotin has been applied to the (vegetable) fibre by the vat process. This suggests that the usual theory that the dye is fixed on the fibre by mere mechanical enclosure is insufficient; the union between the dye and the fibre must be of a more intimate character. It is impossible to say what is the nature of this union. It is determined, however, to some extent by the conditions under which the vat process is conducted. Thus when calico is printed with a mixture of indigo paste, flour thickening, and olive oil (no alkali or reducing agent), and is steamed for three-quarters of an hour, the dye is fixed as the dull blue "indigo grey"; the colour is not fast like that of the ordinary vat blue, and the indigo reacts at once with sodium ethoxide. The same is true when the dye is used in the form of an alcoholic solution of indigo white (without alkali) or in colloidal solution; in both cases the dye on the fibre is attacked by sodium ethoxide. The theory of a union of some kind between the dye and the fibre also serves to explain the fact that indigo on the fibre loses its fastness to scouring by prolonged steaming. The usual explanation, that the loss depends on sublimation, must be incorrect, since indigotin sublimes at about 290° and is not volatile with steam. The author suggests that the union between the dye and the fibre is loosened by steaming; after six hours the separation is complete and the dye readily forms the yellow additive compound with sodium ethoxide.

C. S.

Nomenclature of the Spirans. DAN RADULESCU (*Ber.*, 1911, **44**, 1023—1026. Compare Baeyer, Abstr., 1901, i, 135).—Spirans or

dispirans are homo- or hetero-cyclic compounds containing two rings with a carbon atom common to both; trispirans contain three such rings. Stereochemically the planes of the two rings may be imagined as cutting at right angles. Each ring retains its usual name and the position which the carbon atom common to both rings occupy is indicated. Thus $C_6H_4<^{CH_2}_{CO-}>C<^{CO-}_{CH_2}>C_6H_4$ is bishydrindone-(2:2-) spiran.

By the reduction of ethyl di-*o*-nitrobenzylmalonate, biscarbostyril-spiran, $C_6H_4<^{N:C(OH)}_{CH_2 \text{———}}>C<^{C(OH):N}_{CH_2 \text{———}}>C_6H_4$, is obtained in lustrous, snow-white plates, m. p. above 400° (compare Lellmann and Schleich, Abstr., 1887, 490). It partly sublimes and dissolves in alcoholic potassium hydroxide, being precipitated unchanged by acids. The *chloride* was obtained by the action of phosphorus pentachloride and oxychloride in crystalline flakes; on reduction with hydrogen iodide, 2-*hydroxydihydroquinoline-dihydroquinoline*-(3 : 3)-*spiran* is formed as a greenish-yellow, crystalline powder.

By condensation of dibenzylmalonyl chloride (colourless needles, m. p. 69°, b. p. 225—227°/13 mm.), *bis*-1-*hydrindone*-(2 : 2)-*spiran* is formed. This crystallises in colourless, short, well-formed prisms from benzene or in long needles from amyl alcohol, m. p. 173°. E. F. A.

Preparation of Salt-like Compounds from Toluenesulphonamides and 1-Phenyl- or 1-*p*-Tolyl-2 : 3-dimethyl-5-pyrazolone. ARNOLD VOSWINKEL (D.R.-P. 229814).—When *o*- or *p*-toluenesulphonamide and 1-phenyl- or 1-tolyl-2 : 3-dimethyl-5-pyrazolone are fused together in molecular proportions, crystalline salt-like substances of therapeutic value are obtained.

The *product* from *o*-toluenesulphonamide and 1-phenyl-2 : 3-dimethyl-5-pyrazolone has m. p. 102°, whilst that from *p*-toluenesulphonamide forms prismatic crystals, m. p. 95°. These substances are sparingly soluble in cold, and are rapidly decomposed by boiling water (or alkali) into their components. F. M. G. M.

Hydantoins. Synthesis of Phenylalanine and of Tyrosine. I. HENRY L. WHEELER and CHARLES HOFFMAN (*Amer. Chem. J.*, 1911, **45**, 368—383).—This investigation was undertaken with the object of studying various hydantoin derivatives for synthetical purposes. It has been found that hydantoin condenses readily with aldehydes, and that excellent yields of the products are obtained by boiling hydantoin with aldehydes in presence of glacial acetic acid and anhydrous sodium acetate. Benzylidenehydantoin (Ruhemann and Stapleton, Trans., 1900, 77, 246) can be thus obtained in a yield of 70—80% of the theoretical.

When benzylidenehydantoin is reduced with hydriodic acid, 4-*benzylhydantoin* (*phenylalaninehydantoin*), $CH_2Ph\cdot CH<^{CO-NH}_{NH\cdot CO}$, m. p. 188—190°, is obtained, which forms flat, lancet-shaped crystals; a small quantity of phenylalanine is simultaneously produced. Benzylhydantoin can also be prepared by evaporating a solution of

phenylalanine and potassium cyanate, and warming the residue with dilute hydrochloric acid. On reducing benzylidenehydantoin with aluminium amalgam, an amorphous *aluminium* compound,

$$C_{10}H_{12}O_3N_2,3Al(OH)_3,$$

is produced, together with benzylhydantoin and benzylhydantoic acid. 4-Benzylhydantoic acid (α-carbamido-β-phenylpropionic acid) (Dakin, Abstr., 1909, ii, 685) can be readily obtained by boiling benzylhydantoin with dilute sodium hydroxide. When 4-benzylhydantoin is reduced with hydriodic acid or boiled with barium hydroxide and water, phenylalanine is produced; in one experiment with barium hydroxide, 73% of the hydantoin was converted into phenylalanine and 23·7% into benzylhydantoic acid.

Anisylidenehydantoin, $OMe\cdot C_6H_4\cdot CH{:}C<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix}$, m. p. 243—244° (decomp.), forms brownish-yellow prisms, and, when boiled with alkali hydroxide, yields methyl *p*-hydroxyphenylpyruvate; its *bromo*-derivative, m. p. 247°, crystallises in long, pale yellow needles. When anisylidenehydantoin is boiled for several hours with hydriodic acid, it is converted into tyrosine, together with a small quantity of 4-*p*-hydroxybenzoylhydantoin, but if the mixture is boiled for only one hour, the latter compound is produced in a yield of about 80% of the theoretical. 4-p-*Hydroxybenzylhydantoin* (*tyrosinehydantoin*),

$$OH\cdot C_6H_4\cdot CH_2\cdot CH<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix},$$

m. p. 257—258° (decomp.), forms small, colourless prisms. A tyrosinehydantoin has been obtained by Blendermann (Abstr., 1883, 818), which has m. p. 275—280°, and crystallises in yellow needles; it is suggested that this substance may be an optically active isomeride of the compound now described. 4-*p*-Hydroxybenzylhydantoic acid (tyrosinehydantoic acid) can be obtained by boiling tyrosinehydantoin with dilute alkali hydroxide, but is best prepared by the action of potassium cyanate on tyrosine. The latter method was employed by Jaffé (*Zeitsch. physiol. Chem.*, 1882, 7, 310), but he failed to obtain a pure product. The pure compound has m. p. 172° (decomp.), crystallises in prisms, and when boiled with dilute hydrochloric acid is converted into tyrosinehydantoin. If tyrosinehydantoin is boiled with barium hydroxide and water, tyrosine is produced.

Piperonylidenehydantoin, $CH_2{:}O_2{:}C_6H_3\cdot CH{:}C<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix}$, m. p. 245°, forms clusters of yellow prisms.

Furfurylidenehydantoin, $C_4H_3O\cdot CH{:}C<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix}$, m. p. 232°, crystallises in dark yellow prisms, and gives an intense green coloration with concentrated sulphuric acid.

3 : 5-*Dichloro-4-hydroxybenzylidenehydantoin*,

$$OH\cdot C_6H_2Cl_2\cdot CH{:}C<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix},$$

m. p. 300° (decomp.), forms clusters of long, slender, pale yellow needles, and yields an orange-coloured *ammonium* salt.

p-*Nitrobenzylidenehydantoin*, $NO_2\cdot C_6H_4\cdot CH:C<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix}$, m. p. 254° (decomp.), crystallises in lemon-yellow prisms, and dissolves in *N*-potassium hydroxide to form a blood-red solution.

1-Phenylhydantoin condenses with anisaldehyde with formation of 1-*phenyl*-4-*anisylidenehydantoin*, $OMe\cdot C_6H_4\cdot CH:C<\begin{matrix}CO-NPh\\ NH\cdot CO\end{matrix}$, m. p. 251°, which crystallises in small, yellow prisms. When 3-phenylhydantoin and 1 : 3-diphenylhydantoin are treated in the same way, condensation does not take place. E. G.

Hydantoins. II. Aldehyde Condensation Products of Phenylthiohydantoins. Henry L. Wheeler and Charles A. Brautlecht (*Amer. Chem. J.*, 1911, **45**, 446—458).—It has been shown (preceding abstract) that hydantoin condenses readily with aldehydes in presence of glacial acetic acid and anhydrous sodium acetate, and that 1-phenylhydantoin behaves in a similar manner, whilst 3-phenyl- and 1 : 3-diphenyl-hydantoin do not undergo condensation. Since it seemed probable that the presence of the 3-phenyl group prevented condensation from taking place, a study has been made of the behaviour of 2-thio-1-phenylhydantoin, 2-thio-3-phenylhydantoin, and 2-thio-1 : 3-diphenylhydantoin with aldehydes under similar conditions. It has been found that all these compounds yield condensation products, and that 2-thio-1-phenylhydantoin reacts more readily than hydantoin or 1-phenylhydantoin. The compounds obtained from 2-thio-1-phenylhydantoin and 2-thio-3-phenylhydantoin yield 2-alkylthiol derivatives when warmed with an alkyl halide in presence of sodium alkyloxide.

2-*Thio*-1-*phenyl*-4-*benzylidenehydantoin*, $CHPh:C<\begin{matrix}CO-NPh\\ NH\cdot CS\end{matrix}$, m. p. 204°, forms yellow prisms, and is soluble in about 60 parts of boiling alcohol. 2-*Methylthiol*-1-*phenyl*-4-*benzylidenehydantoin*,

$$CHPh:C<\begin{matrix}CO\cdot NPh\\ N{=}C\cdot SMe\end{matrix},$$

m. p. 150°, crystallises in cream-coloured needles or octahedral pyramids. The corresponding 2-*ethylthiol* derivative, m. p. 123°, forms straw-coloured needles; the 2-*benzylthiol* derivative, m. p. 178—179°, crystallises in nearly colourless needles, and is soluble in about 890 parts of alcohol at 22° and in 137 parts of boiling alcohol. When these thiol derivatives are boiled with hydrochloric acid and alcohol, mercaptan is evolved, and 1-*phenyl*-4-*benzylidenehydantoin*, $CHPh:C<\begin{matrix}CO-NPh\\ NH\cdot CO\end{matrix}$, m. p. 243°, is produced, which forms cream-coloured prisms or diamond-shaped blocks.

2-*Thio*-1-*phenyl*-4-*anisylidenehydantoin*,

$$OMe\cdot C_6H_4\cdot CH:C<\begin{matrix}CO-NPh\\ NH\cdot CS\end{matrix},$$

m. p. 214°, crystallises in long, lemon-yellow needles, and is soluble in about 124 parts of boiling alcohol; its *sodium* salt has m. p. about

280° (decomp.). 2-*Ethylthiol*-1-*phenyl*-4-*anisylidenehydantoin*, m. p. 138—139°, forms yellow needles, and, when boiled with hydrochloric acid and alcohol, yields mercaptan and 1-phenyl-4-anisylidenehydantoin.

2-*Thio*-1-*phenyl*-4-*cinnamylidenehydantoin*,

$$CHPh{:}CH{\cdot}CH{:}C\begin{cases}CO-NPh\\ NH{\cdot}CS\end{cases},$$

m. p. 272—273°, forms long, flat, orange-coloured prisms, and is soluble in about 305 parts of boiling alcohol.

2-*Thio*-1-*phenyl*-4-*piperonylidenehydantoin*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}C\begin{cases}CO-NPh\\ NH{\cdot}CS\end{cases},$$

m. p. 222—223°, crystallises in yellow plates; its *potassium* salt forms long, yellow needles.

2-*Thio*-1-*phenyl*-4-p-*nitrobenzylidenehydantoin*,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}C\begin{cases}CO-NPh\\ NH{\cdot}CS\end{cases},$$

m. p. 278—279°, crystallises in flat, yellow prisms.

2-*Thio*-1-*phenyl*-4-*salicylidenehydantoin*,

$$OH{\cdot}C_6H_4{\cdot}CH{:}C\begin{cases}CO-NPh\\ NH{\cdot}CS\end{cases},$$

m. p. 224—225°, forms pale yellow prisms.

2-*Thio*-1-*phenyl*-4-*furfurylidenehydantoin*,

$$C_4OH_3{\cdot}CH{:}C\begin{cases}CO-NPh\\ NH{\cdot}CS\end{cases},$$

m. p. 233—234°, forms yellow, prismatic blocks.

When ethyl phenylaminoacetate *hydrochloride*, m. p. 119°, is boiled with an alcoholic solution of potassium thiocyanate, 2-*thio*-3-*phenylhydantoin*, $CH_2\begin{cases}CO-NH\\ NPh{\cdot}CS\end{cases}$, m. p. 179—180°, is produced, which forms colourless, transparent prisms.

2-*Thio*-3-*phenyl*-4-*benzylidenehydantoin*, $CHPh{:}C\begin{cases}CO-NH\\ NPh{\cdot}CS\end{cases}$, m. p. 207—208°, crystallises in yellow plates. 2-*Ethylthiol*-3-*phenyl*-4-*benzylidenehydantoin*, m. p. 165—166°, forms yellow prisms, and, when boiled with hydrochloric acid and alcohol, is converted into mercaptan and 3-*phenyl*-4-*benzylidenehydantoin*, $CHPh{:}C\begin{cases}CO-NH\\ NPh{\cdot}CO\end{cases}$, m. p. 223—224° which crystallises in pale yellow plates.

2-*Thio*-3-*phenyl*-4-p-*nitrobenzylidenehydantoin*,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}C\begin{cases}CO-NH\\ NPh{\cdot}CS\end{cases},$$

m. p. 236—237°, forms orange-red prisms.

2-*Thio*-1 : 3-*diphenylhydantoin*, $CH_2\begin{cases}CO-NPh\\ NPh{\cdot}CS\end{cases}$, m. p. 212°, obtained by heating phenylaminoacetic acid or its ethyl ester with phenylthiocarbimide, crystallises in flat, yellow prisms.

2-*Thio*-1 : 3-*diphenyl*-4-*benzylidenehydantoin*, $CHPh\colon C<\begin{matrix}CO-NPh\\ NPh\cdot CS\end{matrix}$, m. p. 193—194°, forms yellow needles.

2-*Thio*-1 : 3-*diphenyl*-4-*anisylidenehydantoin*,

$$OMe\cdot C_6H_4\cdot CH\colon C<\begin{matrix}CO-NPh\\ NPh\cdot CS\end{matrix},$$

m. p. 221—222°, crystallises in yellow needles. E. G.

Interaction of Ethyl Diacetylbutyrate and Hydrazine. Georg Korschun and C. Roll (*Gazzetta*, 1911, 41, i, 186—190. Compare Paal and Kühn, Abstr., 1908, i, 57; Bülow and Filchner, Abstr., 1908, i, 578).—*Ethyl* 3 : 5 : 6-*trimethyl*-4 : 5-*dihydropyridazine*-4-*carboxylate*, $CO_2Et\cdot CH<\begin{matrix}CHMe\cdot CMe\\ CMe=\!=\!=N\end{matrix}>N$, prepared by the action of hydrazine on ethyl $\alpha\beta$-diacetylbutyrate (compare Korschun, Abstr., 1905, i, 373), has m. p. 112·5—113·5°, b. p. about 200°/18 mm., and has the normal molecular weight in freezing benzene.

Ethyl 1-*carbamido*-2 : 3 : 5-*trimethylpyrrole*-4-*carboxylate*,

$$NH_2\cdot CO\cdot NH\cdot N<\begin{matrix}CMe\colon CMe\\ CMe\colon C\cdot CO_2Et\end{matrix}$$

(compare Bülow, Riess, and Sautermeister, Abstr., 1905, i, 660), prepared by the interaction of semicarbazide and ethyl $\alpha\beta$-diacetylbutyrate, forms crystals which do not melt at 210°, and remains unchanged on prolonged boiling with 10% alcoholic potassium hydroxide solution. T. H. P.

Pyrimidines. L. Condensation of Thiocarbamide with Esters of Allylmalonic Acid and Some Alkyl-substituted Allylmalonic Acids. Treat B. Johnson and Arthur J. Hill (*Amer. Chem. J.*, 1911, 45, 356—367).—The γ- and $\gamma\delta$-halogen-substituted propylmalonic acids are unstable (compare Hjelt, Abstr., 1882, 946), and are therefore of limited value for synthetical purposes. The present work was undertaken with the object of obtaining a derivative of allylmalonic acid in which the carboxyl groups would be so linked that lactone formation would not occur after the addition of halogen hydrides or halogens. It was expected that ethyl allylmalonate would react with thiocarbamide to form allylthiobarbituric acid, $CS<\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}>CH\cdot CH_2\cdot CH\colon CH_2$. It has been found, however, that, instead of this compound, a stable, cyclic substance is obtained which is representative of a new class of compounds, the tetrahydrohexathiazoles, of which the simplest member would be

$$S<\begin{matrix}CH=N-CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}.$$

Ethyl benzylallylmalonate and ethyl diallylmalonate do not behave in this way, but condense with thiocarbamide to form the sodium salts of the corresponding acylthiocarbamides, which on treatment with acids are converted into γ-lactones.

Ethyl 2-*amino*-4-*keto*-7-*methyltetrahydrohexathiazole*-5-*carboxylate*,

$S<\begin{matrix}C(NH_2){:}N-CO\\ CHMe\cdot CH_2\cdot CH\cdot CO_2Et\end{matrix}$, m. p. 88—89°, forms pink prisms; it is not desulphurised when warmed with mercuric oxide or lead acetate, and is remarkably stable towards alkali hydroxides. When a solution of this compound in concentrated hydrochloric acid is evaporated to dryness on the water-bath, *γ-thiol*-n-*valerylcarbamide*,

$$SH\cdot CHMe\cdot CH_2\cdot CH_2\cdot CO\cdot NH\cdot CO\cdot NH_2,$$

m. p. 186°, is produced. If the hexathiazole compound is heated with benzyl chloride in presence of sodium ethoxide, *ethyl 2-amino-5-benzyl-7-methyltetrahydrohexathiazole-4-one-5-carboxylate*,

$$S<\begin{matrix}C(NH_2){:}N-CO\\ CHMe\cdot CH_2\cdot C(CH_2Ph)\cdot CO_2Et\end{matrix}$$

m. p. 221°, is obtained, which crystallises in colourless prisms, and, when heated with concentrated hydrochloric acid, gives a quantitative yield of *5-benzyl-5-thiolpropylbarbituric acid*,

$$CO<\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}>C(CH_2Ph)\cdot CH_2\cdot CHMe\cdot SH,$$

m. p. 236°, which forms colourless prisms. On heating the latter compound with 50% potassium hydroxide solution in a sealed tube at 130° and adding excess of hydrochloric acid to the reaction product, *potassium hydrogen benzyl-β-thiolpropylmalonate*,

$$SH\cdot CHMe\cdot CH_2\cdot C(CH_2Ph)(CO_2H)\cdot CO_2K,$$

is produced, and separates in a crystalline form.

Ethyl benzylallylmalonate, $CH_2{:}CH\cdot CH_2\cdot C(CH_2Ph)(CO_2Et)_2$, b. p. 228—230°/60—65 mm., prepared by the action of allyl iodide on ethyl sodiobenzylmalonate or of benzyl chloride on ethyl sodioallylmalonate, is a colourless, viscous oil. On hydrolysis with potassium hydroxide, it yields *α-benzyl-γ-valerolactone-α-carboxylic acid*,

$$\begin{matrix}CHMe\cdot CH_2\cdot C(CH_2Ph)\cdot CO_2H\\ O\text{———————}CO\end{matrix},$$

in the form of a thick syrup; the *silver* salt is described. When this compound is heated with 50% potassium hydroxide solution at 130—150°, it is converted into *benzyl-β-hydroxypropylmalonic acid*, $OH\cdot CHMe\cdot CH_2\cdot C(CH_2Ph)(CO_2H)_2$, which was obtained as an oil; its *silver* salt was prepared. By the action of thiocarbamide on ethyl benzylallylmalonate in presence of sodium ethoxide, *α-benzyl-γ-valerolactone-α-carbonylthiocarbamide*,

$$\begin{matrix}CHMe\cdot CH_2\cdot C(CH_2Ph)\cdot CO\cdot NH\cdot CS\cdot NH_2\\ O\text{———————}CO\end{matrix},$$

m. p. 145—146°, is produced, which forms pale yellow crystals.

α-Allylvalerolactone-α-carbonylthiocarbamide,

$$\begin{matrix}CHMe\cdot CH_2\cdot C(CH_2\cdot CH{:}CH_2)\cdot CO\cdot NH\cdot CS\cdot NH_2\\ O\text{———————}CO\end{matrix},$$

m. p. 134—135°, obtained by the condensation of thiocarbamide with ethyl diallylmalonate, crystallises in cream-coloured plates. When hydrolysed with potassium hydroxide, it yields *β-hydroxypropylallylmalonic acid*, $OH\cdot CHMe\cdot CH_2\cdot C(CH_2\cdot CH{:}CH_2)(CO_2H)_2$, m. p. 120—122° (decomp.), which forms rosettes of small prisms; its *silver* salt was prepared. E. G.

Preparation of Nitrogen Derivatives of Anthraquinones. FRITZ ULLMANN (D.R.-P. 230454).—The patent contains an account of some compounds, certain of which have previously been described (Ullmann and Schalk, this vol., i, 165) *N*-Phenylpyridazonanthrone (*loc. cit.*) forms yellow needles, m. p. 286°. By the interaction of the chloride of anthraquinone-1-carboxylic acid and phenylhydrazine-*p*-sulphonic acid, a *substance* is obtained which crystallises in yellow leaflets. F. M. G. M.

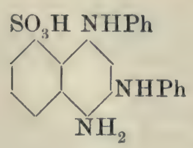
The Halogenation of Indanthren. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 229166).—It is found that indanthren can be readily chlorinated by treatment with aromatic acid chlorides. Indanthren (10 parts) suspended in nitrobenzene is treated with benzoyl chloride (20 parts) and copper powder (0·5 part) and heated at 200—205°, when crystals of *dichloroindanthren* separate from the clear solution; it is very sparingly soluble in organic solvents, but dissolves in concentrated sulphuric acid with an olive-brown colour.

The *compound* obtained from *p*-dihydroxyindanthren and benzoyl chloride is a crystalline powder with metallic lustre and a high chlorine content. F. M. G. M.

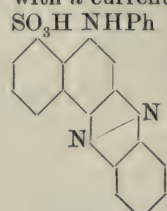
Preparation of 3 : 6-Diaminoacridine. LEOPOLD CASSELLA & Co. (D.R.-P. 230412).—3 : 6-*Diaminoacridine* is prepared by nitrating a cooled sulphuric acid solution of *pp*-diaminodiphenylmethane, and after some hours pouring on to ice; the separated *oo'-dinitro*-pp'-*diaminodiphenylmethane* is reduced with tin and hydrochloric acid, and subsequently heated at 135° during four hours; the diaminoacridine stannichloride is decomposed in the ordinary manner, and the required base extracted with hot water, from which it crystallises in glistening, orange to brown leaflets. F. M. G. M.

Preparation of Azines. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 230456).—Important azine derivatives can be prepared by the action of diazotised aniline on 1 : 3-diarylnaphthylenediamines and their 6-sulphonic or 6 : 8-disulphonic acids.

Aniline is diazotised and coupled with 1 : 3-diphenylnaphthylenediamine-8-sulphonic acid, the *azo*-compound reduced with iron or zinc dust, and the crystalline paste of the reduction *product* (I) treated with ammonium hydroxide and oxidised with a current of air; after



(I.)



(II.)

some time the *azine* (II) is deposited from the deep green solution in the form of a black powder. F. M. G. M.

Preparation of Pyrazine Derivatives. MARTIN LANGE (D.R.-P. 229127).—The interaction of *o*-oxynitroso-compounds with formaldehyde and primary aliphatic amines yields strongly basic pyrazine derivatives according to the general formula:

$$2R^{1}\ll^{O}_{N\cdot OH} + 4CH_2O + R^{11}\cdot NH_2 =$$

$$5H_2O + \begin{matrix} N\!:\!C(OH) \\ | \\ R^{1}\!-\!NR^{11} \end{matrix}\!\!>\!CH\cdot O\cdot CH\!<\!\!\begin{matrix} C(OH)\!:\!N \\ | \\ NR^{11}\!-\!R^{1} \end{matrix},$$

where R^1 is aryl and R^{11} alkyl or substituted alkyl groups.

By the interaction of α-nitroso-β-naphthol, methylamine hydrochloride, and formaldehyde in alkaline solution, the *compound*, (I) $\begin{matrix} N\!=\!=\!C(OH) \\ | \\ C_{10}H_6\cdot NMe \end{matrix}\!\!>\!CH\cdot O\cdot CH\!<\!\!\begin{matrix} C(OH)\cdot N \\ | \\ NMe\!-\!C_{10}H_6 \end{matrix}$, crystallising in colourless needles, m. p. 210°, is obtained. A similar compound, m. p. 228°, in which the group $\cdot CH_2\cdot CO_2H$ replaces the group Me in the above formula, is formed when glycine is substituted for methylamine in the above reaction. Disulphonic and dicarboxy-*derivatives* of (I) are prepared similarly from α-nitroso-β-naphthol-6-sulphonic and -3-carboxylic acids, and by employing α-nitroso-2 : 7-dihydroxynaphthalene, a compound, m. p. 304°, is obtained. F. M. G. M.

Thio-derivatives of Homoantipyrine. FRITZ VON KONEK-NORWALL (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV A I, 234—236).—Antipyrine disulphide, when shaken with mercury in chloroform solution, forms a crystalline compound of the composition $C_{22}H_{22}O_2N_4S_2Hg$. Benzyl, benzoyl, and *p*-nitrophenyl disulphides do not react with mercury. Homoantipyrine (1-phenyl-3-methyl-2-ethylpyrazolone) reacts with sulphur chloride, forming a *monosulphide*, $C_{24}H_{26}O_2N_4S$, which crystallises from benzene in white crystals, m. p. 219—220°, and a *disulphide*, $C_{24}H_{26}O_2N_4S_2$, which forms very pale yellow crystals, m. p. 200°. When the disulphide is shaken in chloroform solution with mercury, a little mercuric sulphide separates, and glistening, pale green crystals of the mercuric *compound*, $C_{24}H_{26}O_2N_4S_2Hg$, are obtained, m. p. 230—231°. The structure of these compounds has not been determined. C. H. D.

Rearrangements. III. GEORG SCHROETER (*Ber.*, 1911, 44, 1201—1209. Compare Abstr., 1909, i, 617, 773).—In extension of his investigations of the reactions by which the chlorides of aromatic ketones are converted through the ketonediazoimide into substituted tetrazoles, the author has examined the behaviour of an aromatic-aliphatic ketone in order to discover whether the aryl or the alkyl group migrates during the reactions. Ketonediazoimides cannot be suitably obtained from the chlorides of aliphatic-aromatic ketones of the type $Ar\cdot CO\cdot CH\colon$, since such chlorides too readily lose hydrogen chloride. Pivalophenone (trimethylacetophenone), however, with phosphorus pentachloride at 140—160°, yields *pivalophenone chloride*, $CMe_3\cdot CCl_2Ph$, b. p. 118—120°/10 mm., which reacts with silver azoimide in boiling amyl ether to form 5-*phenyl*-1-tert.-*butyl*-1 : 2 : 3 : 4-*tetrazole*, $CMe_3\cdot N\!<\!\!\begin{matrix} N\!=\!=\!N \\ \quad | \\ CPh\!:\!N \end{matrix}$, white needles, m. p. 102°. The constitu-

tion of this tetrazole is proved by heating it with 88—90% sulphuric acid at 130° for about two minutes, whereby *iso*butylene and 5-phenyl-1 : 2 : 3 : 4-tetrazole are produced. Consequently the tertiary butyl group has migrated, a result which is rather unexpected, since it is the phenyl group which wanders when acetophenoneoxime experiences the Beckmann transformation and is eliminated when phenyl *tert.*-alkyl ketones are warmed with sodamide (Haller and Bauer, Abstr., 1909, i, 131). Experiments show, however, that when pivalophenoneoxime undergoes the Beckmann change either the alkyl or the aryl group migrates according to the nature of the transforming reagent. Thus in ether with phosphorus pentachloride, the oxime yields products from which benzonitrile can be isolated. Probably the transformation proceeds according to the scheme : $CMe_3\cdot CPh:NOH \rightarrow CMe_3\cdot NH\cdot CPhCl_2 \rightarrow HCl + C_4H_9Cl + C_6H_5\cdot CN$, a view which is supported by the fact that *benz*-tert.-*butylamide*, $CMe_3\cdot NHBz$, m. p. 135·5°, obtained from benzoyl chloride and *tert.*-butylamine, is decomposed by phosphorus pentachloride, yielding hydrogen chloride, *tert.*-butyl chloride, and benzonitrile. When, however, pivalophenoneoxime in glacial acetic acid is heated with hydrogen chloride, it is converted into the *anilide*, $CMe_3\cdot CO\cdot NHPh$, m. p. 132°, of pivalic acid. These results show that caution is necessary in determining the configuration of an oxime from its products of transformation. The author discusses Montagne's criticisms (Abstr., 1910, i, 623) of Schroeter's theory of the course of the Beckmann transformation.

C. S.

1-Methyldeoxyxanthine. Julius Tafel and August Herterich (*Ber.*, 1911, **44**, 1033—1034).—The acid properties of the deoxyxanthines are due to the iminazole ring, and persist so long as this is not methylated ; the susceptibility towards acids is connected with the imino-group in position 3, and disappears when this is methylated. This behaviour is now confirmed in the case of 1-*methyldeoxyxanthine* prepared by electrolytic reduction from 1-methylxanthine (Engelmann, Abstr., 1909, i, 192). This crystallises in reniform aggregates, becomes brown at 240° (decomp 260°). The aqueous solution is neutral. The *sulphate* forms needles in stellate aggregates ; the *oxalate* is a fine crystalline powder ; the *picrate* is obtained in hair-like bent needles.

E. F. A.

Purines. III. 2-Oxy-9-methylpurine and 2 : 8-Dioxy-9-methylpurine. Carl O. Johns (*J. Biol. Chem.*, 1911, **9**, 161—167).—In earlier papers (Abstr., 1909, i, 192 ; this vol., i, 242), 2 : 8-dioxy-6-methylpurine, 2-oxy-6-methylpurine, and 2 : 8-dioxypurine have been described. In continuation of this work, an account is now given of 2-oxy-9-methylpurine and 2 : 8-dioxy-9-methylpurine.

When 6-chloro-2-ethylthiolpyrimidine (Wheeler and Johnson, Abstr., 1903, i, 526) is heated at 100° with an aqueous solution of methylamine, 6-*methylamino-2-ethylthiolpyrimidine*,

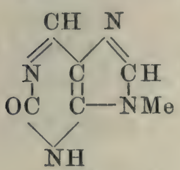
$$N{<}{\begin{matrix}C(SEt)=\!=N\\C(NHMe)\cdot CH\end{matrix}}{>}CH,$$

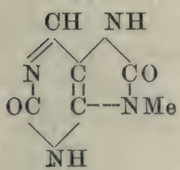
m. p. 55°, is produced, which forms small, stout prisms. On boiling

this substance with concentrated hydrochloric acid, it is converted into 6-*methylamino*-2-*pyrimidone*, $N{<}\begin{matrix}CO\text{———}NH\\C(NHMe)\cdot CH\end{matrix}{>}CH$, m. p. 270° (decomp.), which crystallises in small, stout prisms, and yields a 5-*nitro*-derivative, which forms minute prisms and turns black above 300°. 5-*Amino*-6-*methylamino*-2-*pyrimidone*,

$$N{<}\begin{matrix}CO\text{————————}NH\\C(NHMe)\cdot C(NH_2)\end{matrix}{>}CH,H_2O,$$

obtained by reducing the 5-nitro-compound with ferrous hydroxide, forms slender prisms, darkens at 210°, and decomposes at about 225°. When this compound is heated for an hour with formic acid, the solution evaporated to dryness, and the residue heated at 130—140°, 2-*oxy*-9 *methylpurine* (annexed formula) is produced, which forms long, slender prisms containing $1H_2O$, turns brown at about 290°, decomposes at about 310°, and gives a brilliant murexide reaction.





If a mixture of 5-amino-6-methylamino-2-pyrimidone and carbamide is heated for an hour at 150—160°, 2 : 8-*dioxy*-9-*methylpurine* (annexed formula) is obtained, which crystallises in minute prisms, does not melt below 315°, and yields the murexide reaction.

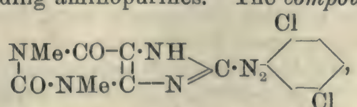
E. G.

Action of Nitriles on Cyanoguanidine. ADRIANO OSTROGOVICH (*Atti. R. Accad. Lincei*, 1911, [v], 20, i, 249—252. Compare this vol., i, 332).—The 4 : 6-diamino-2-methyl-1 : 3 : 5-triazine previously described may also be obtained (yield about 60%) by heating together cyanoguanidine and acetonitrile in a sealed tube for three hours at 225—230°; ammeline is also formed as a secondary product. The corresponding phenyl derivative is obtained by heating cyanoguanidiue with benzonitrile for four or five hours in a sealed tube at 190—200°; in this case also some ammeline is produced.

It appears likely that the reaction can be extended to other cases, and further, diguanide may be employed instead of cyanoguanidine, although the yields obtained in this case are poor.

R. V. S.

Preparation of 8-Aminopurine Derivatives. KALLE & Co. (D.R.-P. 230401. Compare Burian, Abstr., 1904, i, 354).—8-Amino-2 : 6-dioxypurine derivatives have previously been prepared by treating the 8-chloro-derivatives with ammonia at a high temperature; it is now found that purines which are unsubstituted in positions 7 and 8 will couple energetically with diazonium salts, and by subsequent reduction yield the corresponding aminopurines. The *compound*,



glistening, red needles, is prepared by diazotising 2 : 5-dichloroaniline

and coupling it in alkaline solution with theophylline; on reduction a quantitative yield of 8-aminotheophylline is obtained.

F. M. G. M.

New Method of Preparation of Azo-compounds. ROBERT STOLLÉ and J. LAUX (*Ber.*, 1911, 44, 1127—1134).—Halogen compounds of the types: $CAr_2X\cdot CX{:}N\cdot N{:}CX\cdot CArX$ and

$$CAr_2X\cdot C\Big<\begin{matrix}N\cdot N\\ -Y-\end{matrix}\Big>C\cdot CAr_2X$$

(where X = halogen, and Y = S, :NH, :NR or ·N:N·) when shaken with mercury lose halogen from the $\alpha:\zeta$-positions, with the formation of $CAr_2{:}CX\cdot N{:}N\cdot CX{:}CAr_2$ and $CAr_2{:}C\Big<\begin{matrix}N{:}N\\ -Y-\end{matrix}\Big>C{:}CAr_2$ respectively. The azo-compounds thus obtained readily combine with halogens, the addition taking place in the $\alpha:\zeta$-position.

s-*Bi-diphenylacetylhydrazide*, $CHPh_2\cdot CO\cdot NH\cdot NH\cdot CO\cdot CHPh_2$, prepared by the addition of an ethereal solution of diphenylacetyl chloride to a mixture of hydrazine hydrate and sodium carbonate in aqueous solution, crystallises in slender needles, m. p. 297°. It reacts with phosphorus pentachloride in carbon tetrachloride solution, yielding *bis-diphenylacetylhydrazide chloride*, $CHPh_2\cdot CCl{:}N\cdot N{:}CCl\cdot CHPh_2$, which forms slender, colourless needles, and, when heated with phosphorus pentachloride at 120—130°, is transformed into *bis-diphenylchloroacetylhydrazide chloride*, $CPh_2Cl\cdot CCl{:}N\cdot N{:}CCl\cdot CPh_2Cl$, crystallising in colourless leaflets, m. p. 164°.

Azodiphenylchloroethylene (*bisdiphenylchlorovinyldi-imide*),

$$CPh_2{:}CCl\cdot N{:}N\cdot CCl{:}CPh_2,$$

prepared by shaking a benzene solution of the last-named compound with mercury, forms lustrous, brick-red crystals, m. p. 236°; it combines with chlorine, yielding the original hydrazide chloride, and with bromine to form *bisdiphenylbromoacetylhydrazide chloride*, m. p. 175°; the *additive* compound with hydrochloric acid has m. p. 145°.

2 : 5-*Dibenzhydryl*-1 : 3 : 4-*oxadiazole*, $CHPh_2\cdot C\Big<\begin{matrix}N\cdot N\\ -O-\end{matrix}\Big>C\cdot CHPh_2$, is obtained by heating *s*-bisdiphenylacetylhydrazide with phosphoryl chloride for several days in benzene solution; it crystallises in slender needles, m. p. 162°, and, when heated with phosphorus pentachloride in benzene solution, yields *di-ω-chloro*-2 : 5-*dibenzhydryl*-1 : 3 : 4-*oxadiazole*, $CPh_2Cl\cdot C\Big<\begin{matrix}N\cdot N\\ -O-\end{matrix}\Big>C\cdot CPh_2Cl$, which forms stout, octahedral crystals, m. p. 165°.

2 : 5-*Didiphenylmethylenedihydro*-1 : 3 : 4-*oxadiazole*,

$$CPh_2{:}C\Big<\begin{matrix}N{:}N\\ -O-\end{matrix}\Big>C{:}CPh_2,$$

obtained by shaking bisdiphenylchloromethyl-1 : 3 : 4-furazan with mercury in benzene solution for several days, forms dark brownish-red crystals, having a green fluorescence, m. p. 174°; it combines with chlorine, forming the original di-ω-chloro-1 : 3 : 4-oxadiazole, and with bromine, yielding *di-ω-bromo*-2 : 5-*dibenzhydryl*-1 : 3 : 4-*oxadiazole*, $C_{28}H_{20}ON_2Br_2$, which forms colourless crystals, m. p. 179°, and is also

obtained by the bromination of dibenzhydryl-1 : 3 : 4-oxadiazole in the presence of phosphorus pentabromide; the *additive* product with hydrochloric acid has m. p. 130°.

1-*Phenyl*-2 : 5 -*dibenzhydryl*-1 : 3 : 4-*triazole*,

$$CHPh_2\cdot C{<}{\substack{N\cdot N\\NPh}}{>}C\cdot CHPh_2,$$

prepared by heating bisdiphenylacetylhydrazide chloride with aniline at 150°, crystallises in slender needles, m. p. 215°; on chlorination this yields *di-ω-chloro*-1-*phenyl*-2 : 5-*dibenzhydryl*-1 : 3 : 4-*triazole*,

$$CPh_2Cl\cdot C{<}{\substack{N\cdot N\\NPh}}{>}C\cdot CPh_2Cl,$$

which crystallises in colourless cubes, m. p. 204° (decomp.), and gives a deep bluish-violet coloration when shaken with mercury in benzene solution.

3 : 6-*Dibenzhydryldihydro*-1 : 2 : 4 : 5-*tetrazine*,

$$CHPh_2\cdot C{<}{\substack{N\text{——}N\\NH\cdot NH}}{>}C\cdot CHPh_2,$$

is obtained by the interaction of bisdiphenylacetylhydrazide chloride and hydrazine hydrate in benzene solution; it melts at 190°, becoming red in colour, and is oxidised with amyl nitrite in alcoholic solution to 3 : 6-*dibenzhydryl*-1 : 2 : 4 : 5-*tetrazine*,

$$CHPh_2\cdot C{<}{\substack{N\cdot N\\N:N}}{>}C\cdot CHPh_2;$$

this crystallises in slender, violet needles, m. p. 172°. F. B.

Preparation of Naphtha-anthraquinoneazines. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 230005).—It is found that the azo-derivatives of anthraquinonyl-β-naphthylamine are converted by condensing agents (such as sulphuric acid) into the corresponding naphtha-anthraquinoneazines. Benzeneazo-α-anthraquinonyl-β-naphthylamine (prepared from α-chloroanthraquinone and benzeneazo-β-naphthylamine) is dissolved in 80% sulphuric acid and heated during several hours at 100°; on dilution with water the *azine* separates in crystalline form. F. M. G. M.

Preparation of Arylsulphodiazoimino-derivatives. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 229247).—Arylsulphodiazoimino-derivatives are prepared by coupling diazotised aniline, *p*-nitroaniline, and *o*:*o*-dianisidine with *p*-toluenesulphonylaniline-*m*- or -*p*-sulphonic acids respectively. The *sodium* salts (two series owing to the replacability of the iminic hydrogen by metals) are colourless, crystalline needles or powders, the free acids are sparingly soluble in water, but the introduction of two or more sulphonic groups in the molecule yields soluble and readily crystallisable compounds.

The *products* from *p*-nitroaniline, and from *o*:*o*-dianisidine with *p*-toluenesulphonylaniline-*m*-sulphonic acid separate in brown nodules, whilst benzeneazo-α-naphthylamine when diazotised and coupled in the same manner yields a similar product. Treatment with concentrated sulphuric acid removes the *p*-toluenesulphonyl residue. F. M. G. M.

Diazoamino- and Aminoazo-derivatives Obtained from Aminomethylenedioxybenzene. EFISIO MAMELI (*7th Intern. Congr. App. Chem.*, 1909, Sect. IV B, 101—107. Compare Abstr., 1909, i, 854).—The diazo-compound of aminomethylenedioxybenzene yields with aniline a mixture of aminoazo- and diazoamino-derivatives, whilst from diazobenzene and aminomethylenedioxybenzene only the aminoazo-derivative is formed. Aminomethylenedioxybenzene reacts with the diazonium salts prepared from α- and β-naphthylamine, giving aminoazo-derivatives, and aminoazo-derivatives are also obtained from the diazo-compound of aminomethylenedioxybenzene and α- and β-naphthylamine. Finally, the diazo-compound of aminomethylenedioxybenzene reacts with aminomethylenedioxybenzene, yielding an aminoazo-derivative identical with that formed by the action of nitrous acid on an excess of aminomethylenedioxybenzene.

*Benzeneazo-*4-*amino-*1 : 2-*methylenedioxybenzene*,

$$CH_2{:}O_2{:}C_6H_2(NH_2){\cdot}N_2Ph,$$

has m. p. 130°.

4-*Amino-*1 : 2-*methylenedioxybenzene-α-azonaphthalene*,

$$CH_2{:}O_2{:}C_6H_2(NH_2){\cdot}N_2{\cdot}C_{10}H_7,$$

has m. p. 151°, whilst the analogous derivative of *β-diazonaphthalene* has m. p. 175°.

1 : 2-*Methylenedioxybenzenediazoaminobenzene*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}N_3H{\cdot}Ph,$$

has m. p. 148—149°. Along with it a small quantity of an *aminoazo*-compound is formed,

*α-Aminonaphthalene-*4-*azo-*1 : 2-*methylenedioxybenzene*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2,$$

has m. p. 189—190°, and the *β-derivative*, m. p. 142—144°.

*Aminoazo-*1 : 2-*methylenedioxybenzene*,

$$CH_2{:}O_2{:}C_6H_2(NH_2){\cdot}N_2{\cdot}C_6H_3{:}O_2{:}CH_2,$$

has m. p. 210—215°.

The aminoazo-derivatives yields salts, some of which are fairly stable, and acetyl and benzoyl compounds have also been prepared. Both aminoazo- and diazoamino-derivatives dye wool and silk, and cotton when mordanted ; in most cases the colours are fast to washing and to light. R. V. S.

Yeast Nucleic Acid. IV. PHOEBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1911, 44, 1027—1032. Compare Abstr., 1909, i, 620, 686 ; this vol., i, 96).—Compounds analogous to inosic and guanylic acid of the type $PO(OH)_2{\cdot}O{\cdot}C_5H_8O_4,C_5H_4ON_5$, are termed nucleotides, and the molecule of yeast-nucleic acid is composed of four such nucleotides. By boiling nucleic acid with 2% sulphuric acid for two hours a mixture of the pyrimidine nucleotides was obtained, namely, cytidine nucleotide, $PO(OH)_2{\cdot}O{\cdot}C_9H_{12}O_4N_3$, and uridine nucleotide, $PO(OH)_2{\cdot}O{\cdot}C_9H_{11}O_5N_2$. This was hydrolysed with ammonia and cytidine isolated as nitrate ; the filtrate from this was evaporated to dryness and benzoylated, when dibenzoyluridine was obtained. Uridine was also isolated after hydrolysis from the residues without the addition of nitric acid, which can conceivably bring about its formation from cytidine. A comparison of uridine obtained as above with that

prepared by the action of nitrous acid on cytidine showed them to be identical. E. F. A.

Comparative Observations on the Composition and Cleavage of Different Kinds of Silk. XII. The Monoamino-acids from the "Gelatin" of Indian Tussore Silk. FRIEDRICH WILHELM STRAUCH (*Zeitsch. physiol. Chem.*, 1911, **71**, 365—366).—The gelatin obtained from Indian tussore silk contained 25% of ash. One hundred grams of ash-free substance yielded: glycine, 1·5; alanine, 9·8; leucine, 4·8; serine, 5·4; aspartic acid, 2·8; glutamic acid, 1·8; phenylalanine, 0·3; tyrosine, 1·0; and proline, 3·0 grams.

W. D. H.

Action of Pepsin and Hydrochloric Acid on Elastin and other Proteins. III. EMIL ABDERHALDEN and FRANZ WACHSMUTH (*Zeitsch. physiol. Chem.*, 1911, **71**, 339—364).—Further details as to time, etc., are given in relation to the action of elastin and pepsin. Some forms of horny structure behave like elastin in adsorbing pepsin. W. D. H.

Action of the Enzymes of Gastric Juice. II. EMIL ABDERHALDEN and FRIEDRICH W. STRAUCH (*Zeitsch. physiol. Chem.*, 1911, **71**, 315—338. Compare Abstr., 1910, i, 795).—Elastin takes up pepsin from gastric juice, and when then placed in distilled water at 37°, undergoes digestion; if pancreatic juice replaces the water, it is more rapidly digested, and the same occurs if sodium hydroxide solution is employed. The adsorbed pepsin appears to be protected and able to work in an unusual medium. Water removes some of the adsorbed enzyme from the elastin. Elastin also adsorbs propepsin, rennet, and trypsin. Both the peptic and rennetic activities of the gastric juice are destroyed by shaking, but the lessening of the two actions does not appear to be quite parallel. By the elastin method a proteolytic enzyme can be extracted from fæces.

W. D. H.

The Stimulating Effect of Chloride of Calcium and of Intestinal Mucous Membrane Extract on the Action of Trypsin. EBEL HEKMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 1002—1012).—Calcium chloride increases the activity of trypsin which contains no trypsinogen, and this action is to be distinguished from the activating effect on the latter. Extracts of mucous membrane also increase the activity by trypsin, even after they have been boiled. In addition, therefore, to enterokinase, which activates trypsinogen and is not heat stable, another substance is present in the extract of mucous membrane which promotes tryptic digestion by accelerating the action on the activated trypsin. S. B. S.

Bacterial Proteases. KURT MEYER (*Biochem. Zeitsch.*, 1911, **32**, 274—279).—The proteases obtained from *Bacillus prodigiosus* and *B. pyocyaneus* exhibit their maximum action in faintly alkaline

solution (hydrogen ion concentration $= 10^{-7 \cdot 2}$), and these enzymes are therefore classed with the tryptases.

These enzymes are not destroyed when their solutions are boiled, but are rendered completely inactive when heated between 56° and 85°, and the activity is not restored by further heating to 100°, as happens in the case of staphylolysin. The proteases will not bring about the digestion of protein at 100°. W. J. Y.

Bacterial Anti-proteases. KURT MEYER (*Biochem. Zeitsch.*, 280—286).—By immunising rabbits with solutions of the proteases from *Bacillus prodigiosus* and *B. pyocyaneus*, sera were obtained which contained anti-substances to these enzymes. These anti-substances withstood heating for half an hour at 75°, but were destroyed at 100°, so that a mixture of protease and antiprotease was rendered active again by heating at 100°. They were precipitated with the globulin fraction of the serum, and were weakened by extraction with light petroleum.

When the protease was added fractionally to the anti-substance, the Danysz effect was not observed. The proteases were not completely bound by the anti-substance, since the enzyme was able to bring about digestion to a slight extent even in the presence of excess.

These anti-substances would not inhibit the action of other bacterial proteases nor of pancreatic trypsin; they are therefore specific.

W. J. Y.

Action of Invertase on Polysaccharides Derived from Lævulose. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1911, **152**, 1060—1062).—Sucrose, raffinose, gentianose, and stachyose have the property in common of yielding lævulose and dextrose as products of hydrolysis when acted on by invertase. The order in which these sugars are placed indicates the relative rates at which lævulose is liberated, the first-mentioned being most rapidly decomposed. The marked difference in the rates of hydrolysis suggests that the ferment has to bring about disruption, not only between a single dextrose and lævulose residue, but also, in the case of raffinose, gentianose, and stachyose, between lævulose and the rest of the molecule. In other words, it would appear that the lævulose complex is not the terminal member of a chain of hexoses in these three polysaccharides.

W. O. W.

Organic Chemistry.

New Method for Esterification of Alcohols by Halogen Acids. GEORGES DARZENS (*Compt. rend.*, 1911, **152**, 1314—1317).—A general method for replacing the hydroxyl group by a halogen consists in treating the substance with thionyl chloride or bromide (2 mols.) in presence of a tertiary base (1 mol.). There is but little development of heat, and the reaction is complete in half an hour. Sulphur dioxide may be removed by heating at 80—110°, but this is not always necessary. The process gives yields exceeding 95%, and is stated to be free from the disadvantages associated with the use of a halogen hydride or the employment of phosphorus pentachloride. Dimethyl- and diethyl-aniline are the most suitable bases to use. As examples of its application, the conversion of *iso*amyl alcohol, dichlorohydrin, benzyl carbinol, and cinnamyl carbinol into the corresponding chloro-derivatives is mentioned. The method cannot be applied to phenols. *cyclo*Hexanol is converted into *cyclo*hexene through removal of hydrogen chloride from the unstable chloro-compound.

W. O. W.

Boiling Point of Mixtures of Water and [Ethyl] Alcohol. C. MARILLER (*Bull. Assoc. chim. Sucr. Dist.*, 1911, **28**, 768—770).—The boiling point of mixtures of ethyl alcohol and water, containing 8 to 100% of alcohol, can be represented by means of the formula $t = 78{\cdot}4 + \sqrt{0{\cdot}22\ a.e/a}$, in which e and a denote respectively the percentages of water and alcohol in the mixture boiling at $t°$ under atmospheric pressure.

H. M. D.

Synthesis of Tertiary α-Keto-alcohols. D. GAUTHIER (*Compt. rend.*, 1911, **152**, 1259—1261. Compare this vol., i, 415).—An extension of the reaction previously described to the cyanohydrins of ketones. *β-Methylbutanone-β-ol*, $OH{\cdot}CMe_2{\cdot}COMe$, prepared by the action of magnesium methyl iodide on acetone cyanohydrin (cyano*iso*propyl alcohol), has b. p. 79°/730 mm., and forms a *semicarbazone*, m. p. 180°. This substance is not identical with the compound to which Schmidt and Austin (Abstr., 1903, i, 2) have ascribed the above constitution.

β-Methylpentan-γ-one-β-ol, $OH{\cdot}CMe_2{\cdot}COEt$, has b. p. 96—98°/725 mm. *γ-Methylpentanone-γ-ol*, $OH{\cdot}CMeEt{\cdot}COMe$, has b. p. 94°/729 mm.

W. O. W.

Chemical Action of Light. XIX. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1911, **44**, 1280—1289. Compare Abstr., 1910, i, 299).—A mixture of acetone (1 part) and methyl alcohol (2 parts), after being exposed to the action of light for over one year, was found to contain *iso*propyl alcohol, formaldehyde, ethylene glycol, and *iso*butylene glycol, $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$. The two substances first-named are formed by the interaction of acetone and methyl alcohol:

$$COMe_2 + Me{\cdot}OH = CHMe_2{\cdot}OH + CH_2O,$$

whilst the formation of ethylene glycol and *iso*butylene glycol is due to a condensation of methyl alcohol with formaldehyde and acetone respectively.

Similar results have been obtained by replacing the methyl alcohol by ethyl alcohol. A mixture of acetone and ethyl alcohol, after exposure to light for nine months, gave the following products: (1) diacetyl, which was identified by means of its oxime, m. p. 244° (Fittig, Abstr., 1889, 490, gives 234·5°); (2) *iso*propyl alcohol; (3) *β-methylbutylene βγ-glycol*, $OH\cdot CMe_2\cdot CHMe\cdot OH$; (4) an oil, containing, amongst other substances, trimethylethylene glycol and butylene-βγ-glycol, $OH\cdot CHMe\cdot CHMe\cdot OH$. In order to separate the latter compound, advantage was taken of the fact that it undergoes the pinacolin rearrangement when heated with dilute sulphuric acid at 130° less readily than methylbutylene glycol, which is converted under the same conditions into methyl *iso*propyl ketone. The distillate, after this treatment, was found to contain, besides methyl *iso*propyl ketone, a *liquid*, b. p. 149°, having the composition $C_4H_{10}O_2$. This substance is probably formed from methylbutylene glycol and butylene glycol by the loss of water: $C_5H_{12}O_2 + C_4H_{10}O_2 = 2H_2O + C_9H_{18}O_2$, but whether it is contained in the original mixture or is subsequently produced by the action of sulphuric acid has not been decided.

The βγ-butylene glycol, isolated from the mixture, gave, on treatment with phenylcarbimide, two isomeric *phenylurethanes*, the less soluble one having m. p. 175°, the other, m. p. 201—202°. These have the composition $NHPh\cdot CO\cdot O\cdot CHMe\cdot CHMe\cdot O\cdot CO\cdot NHPh$, and are considered by the authors to be the phenylurethanes of racemic and inactive butylene βγ-glycol. Two *dibenzoyl* derivatives,

$$OBz\cdot CHMe\cdot CHMe\cdot OBz,$$

were also obtained: a solid, crystalline form, m. p. 77° (monoclinic: $a:b:c = 0.4170:1:0.3337$; $\beta = 69°6'$), and a liquid modification, b. p. 217—218°/16 mm.

With *iso*propyl alcohol and acetone the reaction is much simpler; the only product formed by exposing a mixture of these substances, in equal parts, to the action of light for nine months consists of pinacone.

With the object of discovering if a condensation of alcohol with aromatic ketones takes place under the influence of light, similar to that found in the case of acetone, the behaviour of benzophenone in ethyl-alcoholic solution has been re-investigated (compare Abstr., 1901, i, 329), but no evidence of such a condensation has been obtained.

F. B.

Basic Properties of the Oxygen of Ethers. DEMETRIUS E. TSAKALOTOS (*Bull. Soc. chim.*, 1911, [iv], 9, 519—523).—Determinations of the viscosities and densities of mixtures of (1) ethyl ether and acetic acid, and (2) ethyl ether and trichloroacetic acid, indicate that the first two substances do not form additive compounds with each other, whilst the second two form at least one (compare Tsakalotos and Guye, Abstr., 1910, ii, 826). The conclusion is drawn that ethereal oxygen is weakly basic and can only unite with strong acids.

T. A. H.

Catalytic Decomposition of Formic Acid. Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1911, **152**, 1212—1215).—Substances which bring about catalytic decomposition of formic acid may be divided into three classes: (1) Those capable of effecting dehydrogenation; the products in this case contain only traces of formaldehyde. The following act in this way: palladium, platinum, rhodium, reduced copper, nickel and cadmium, zinc and stannous oxides; (2) catalysts effecting dehydration, namely, the oxides of titanium, tungsten, zirconium, aluminium, uranium and silicon; (3) substances acting in the same way as the foregoing, but in addition giving more or less formaldehyde, such as ferrous, manganous, chromic, magnesium, molybdenum, vanadium and glucinum oxides, lime, carbon and Jena glass. Since the nature of the products and their relative proportions depend on the catalyst employed, it is evident that these substances do not act merely by lowering the temperature at which the reactions become possible. W. O. W.

Direct Synthesis of Glycerides. Italo Bellucci and R. Manzetti (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 503—504).—In reply to Gianoli's claim for priority (Sixth Congress of Applied Chemistry, Rome, 1906; this vol., i, 349) to the authors (this vol., i, 259), the latter point out that Scheij (Abstr., 1899, i, 667) was the first to synthesise glycerides under reduced pressure. T. H. P.

The Systems: Fat–Alcohol. Albert J. J. Vandevelde (*Bull. Soc. chim. Belg.*, 1911, **25**, 210—216).—Butter-fat, cocoanut oil, and olive oil were separately brought into contact with different proportions of 94% alcohol at 37° until equilibrium was attained, and the composition of the fatty and alcoholic layers was then determined. Similar experiments were also made with a mixture of butter-fat and cocoanut oil. H. M. D.

Action of Ultra-violet Light on Lactic Acid. Marc Landau (*Compt. rend.*, 1911, **152**, 1308—1309. Compare Berthelot and Gaudechon, this vol., ii, 170; Euler, *ibid.*, ii, 452).—In addition to the liberation of gases when lactic acid is exposed to ultra-violet light, other changes occur involving the production of ethyl alcohol, pyruvic acid, and traces of an unidentified substance which reduces ammoniacal silver nitrate in the cold. W. O. W.

Oxidation of Higher Acetylenic Aliphatic Acids. Albert Arnaud and V. Hasenfratz (*Compt. rend.*, 1911, **152**, 1603—1606. Compare Abstr., 1902, i, 342—343).—In the oxidation of stearolic and tariric acids by nitric acid, the chain is broken between the two carbonyl groups of the diketonic acid which represents the first stage of oxidation. When potassium permanganate is employed, however, one carbonyl group is eliminated as carbon dioxide. This follows from the observation that on treatment with alkaline permanganate, stearolic acid gives nonoic and octoic acids (38%) with suberic and azelaic acids (53%), whilst tariric acid yields lauric and undecoic acids (55%) with glutaric and adipic acids (25%). W. O. W.

Studies on Tautomerism. IV. Desmotropy of Acetoacetic Ester. LUDWIG KNORR, O. ROTHE, and H. AVERBECK (*Ber.*, 1911, **44**, 1138—1157).—The ketonic and enolic forms of ethyl acetoacetate have been isolated in a pure condition and their transformations studied. The ketonic ester is sparingly soluble in organic solvents at a low temperature, and therefore crystallises when its solutions are strongly cooled. It was isolated by cooling its solution in alcohol or a mixture of alcohol and ether to $-78°$, and washing the crystals thus obtained with light petroleum or methyl ether until free from the enolic form, in a specially constructed apparatus, a sketch of which is given. All operations must be carried out in the complete absence of moisture. The ketonic ester crystallises in prisms or needles, which may be kept for a long time at a low temperature without undergoing any change. At the ordinary temperature it is slowly transformed into the equilibrium mixture, the change in the absence of catalytic influences being complete in the course of several weeks. Small quantities may be distilled in the vacuum of the cathode light practically unchanged. It has b. p. 40—41°/2 mm., n_D^{10} 1·4225, and solidifies at $-39°$, whereas the equilibrium mixture solidifies at $-45°$ to $-43°$, and has b. p. 39—40°/2 mm., n_D^{10} 1·4230 to 1·4232. At the ordinary temperature, it gives the ferric chloride reaction like the equilibrium mixture, but this is ascribed to enolisation induced by the ferric chloride. At low temperatures the enolisation takes place less rapidly, and in these circumstances comparative tests show that the red coloration with ferric chloride is developed much more slowly in the case of the ketonic ester than with the equilibrium mixture.

The enolic ester is obtained by treating a suspension of ethyl sodioacetoacetate in light petroleum with gaseous hydrogen chloride, in quantity just insufficient for complete decomposition, filtering from sodium chloride, and evaporating the filtrate as rapidly as possible under strongly diminished pressure, all operations being carried out at $-78°$ and in the complete absence of moisture. A sketch of the apparatus employed is given.

The enolic ester is a colourless oil, having an agreeable fruity odour; it has D_4^{10} 1·0119, n_D^{10} 1·4480, and solidifies in liquid air to a glassy mass, which soon becomes crystalline. In a high vacuum and in small quantities, it distils at about 33° without undergoing appreciable change. Its enolic nature is shown by a much more rapid development of the ferric chloride reaction than is the case with the ketonic ester. In ethereal solution at $-78°$, it gives at once an intense coloration with ethereal ferric chloride. Reasons are given in favour of the cis-configuration, $\begin{array}{l}\mathrm{H-C\cdot CO_2Et}\\ \quad \| \\ \mathrm{Me\cdot C\cdot OH}\end{array}$, for the ester.

A large number of mixtures of the ketonic and enolic esters have been prepared, and their refractive indices determined; from the results thus obtained it is found that, at the equilibrium point, ethyl acetoacetate contains 2% of the enolic form (compare Hantzsch, Abstr., 1910, i, 811; K. H. Meyer, this vol., i, 350).

At low temperatures the enolic ester may be kept for a long time unchanged. At the ordinary temperature, it is transformed in the

course of ten to fourteen days into the equilibrium mixture, whilst at 100° the transformation is complete in one minute. The velocity of transformation has been determined refractometrically, and it is found to be enormously increased by the catalytic influence of both acids and bases. Contact with gaseous hydrogen chloride, soft alkali glass, and even exposure to air, transform the enolic ester into the equilibrium mixture in the course of a few seconds or minutes. In solution, the velocity of transformation at the ordinary temperature also increases, but diminishes rapidly with fall of temperature.

The influence of temperature on the equilibrium between the ketonic and enolic forms has been investigated by heating ethyl acetoacetate at various temperatures up to 181°, and then rapidly cooling, but no displacement of the equilibrium could be detected. Refractometric measurements showed that all specimens thus treated contained 2% of the enolic modification.

The equilibrium between the ketonic and enolic esters in the form of vapour varies, however, with the temperature and pressure. When ethyl acetoacetate is distilled under ordinary pressure and the vapour rapidly cooled, a distillate containing 10% of the enolic form was obtained, whilst by distilling slowly under diminished pressure and cooling the vapour rapidly to $-78°$, the proportion of enolic ester rises to 27—39%, and remains constant until the end of the distillation. According to the authors, the greater proportion of the enolic form in the distillate is due to its greater vapour pressure; it therefore distils over more rapidly, and since the equilibrium thus disturbed is quickly restored at the temperature of the distillation, the enolic ester is continuously replenished in the distillation flask. The distilled ester is far more rapidly transformed into the equilibrium mixture than the enolic ester, prepared from ethyl sodioacetoacetate. The view is expressed that this is due to the formation during the distillation of the trans-enolic ester, which has a greater velocity of transformation into the ketonic form than the cis-isomeride.

The relative proportions of the ketonic and enolic forms in equilibrium in various solvents have also been determined; the values obtained for the percentage of enolic ester vary from 2% in light petroleum to 31% in hexane.

By strongly cooling solutions of many other tautomeric substances, one of the forms crystallises out, whilst in other cases a separation may be effected by freezing and pressing out. F. B.

Action of Thionyl Chloride in Presence of a Tertiary Base on Esters of Hydroxy-acids. Georges Darzens (*Compt. rend.*, 1911, 152, 1601—1603. Compare this vol., i, 513).—The method previously described for replacing the hydroxyl group by a halogen has been successfully applied to the esters of hydroxy-acids. Ethyl lactate gave a practically theoretical yield of ethyl α-chloropropionate; pyridine is the best base to employ in this case. Ethyl l-malate has been transformed into ethyl d-chlorosuccinate; less racemisation takes place than when phosphorus pentachloride is employed, and the product has $[\alpha]_D^{20} + 31{\cdot}20°$, whereas Walden found 27·30°.

In some cases dehydration occurs; thus ethyl *cyclo*hexan-1-ol-1-carboxylate gives ethyl *cyclo*hexenecarboxylate, whilst esters of the type $OH\cdot CRMe\cdot CH_2\cdot CO_2Et$ are converted into the corresponding acrylates. W. O. W.

ψ-Acid Esters in the Mesoxalic Ester Synthesis. RICHARD S. CURTISS and JOHN A. KOSTALEK (*J. Amer. Chem. Soc.*, 1911, **33**, 962—974).—It has been shown by Curtiss (Abstr., 1906, i, 480) that when the gases evolved by the action of nitric acid on arsenious oxide are allowed to react with ethyl malonate at $-10°$, ethyl mesoxalate is produced, together with an oily acid substance which was at first supposed to be ethyl *iso*nitrosomalonate, but has now been found to consist of a mixture of acid esters containing nitrogen. From this mixture, ethyl nitromalonate and ethyl dinitroacetate have been separated by means of their potassium salts. The acid esters are colourless oils, whilst their potassium salts are coloured. Ethyl nitromalonate and its salts have been studied by Hantzsch (Abstr., 1907, i, 556), who explains the variation in colour on the basis of differences in structure.

Ethyl dinitroacetate yields potassium salts of two forms, one yellow, which has been described by Bouveault and Wahl (Abstr., 1903, i, 225), and the other red, the latter being known only in solution. The cold aqueous solution of the yellow form is also yellow, but becomes red when heated, and reverts to its original colour on cooling. The yellow form is dimorphous, crystallising in slender, monoclinic prisms or lustrous plates; it decomposes at 194—195°. On reduction with tin and hydrochloric acid, it yields ethyl glyoxylate and ammonia. When the potassium salt is heated with methyl or ethyl iodide and 50% alcohol in a sealed tube at 100—110°, a yellow, viscous, unstable oil is produced. The salt reacts more readily with ethyl sulphate, and yields potassium sulphate and nitrite and a mixture of oily products. On boiling potassium ethyl dinitroacetate (1 mol.) with alcoholic potassium hydroxide (2 mols.), a brilliant yellow *salt* is formed, which is probably a form of dipotassium *aci*-dinitroacetate; it decomposes violently at 210°. The *ammonium* and *silver* salts of ethyl dinitroacetate are described; the *sodium*, *hydrazine*, and *aniline* salts were also prepared.

Potassium ethyl nitromalonate, m. p. 154°, crystallises in dark yellow needles or hexagonal prisms. Hantzsch (*loc. cit.*) obtained a colourless form of this salt by the action of potassium carbonate on the colourless form of the ammonium salt. The ammonium salt, m. p. 151°, obtained by the action of dry ammonia on ethyl nitromalonate at $-10°$, forms pale yellow, prismatic crystals. The white modification dissolves in alcohol or water to form a yellow solution.

If dry ammonia is passed into an ethereal solution of the crude product of the action of nitrogen oxides on ethyl malonate, the salts of ethyl nitromalonate and ethyl dinitroacetate are precipitated. When an excess of ammonia is added, an unstable red oil separates. The filtrate from the ammonium salts yields a crystalline substance, m. p. 50°, which forms flat, colourless needles. E. G.

New Complex Iridium Derivatives: Iridotetrachloro-oxalates and Iridotetrachlorides. ALEXIS DUFFOUR (*Compt. rend.*, 1911, **152**, 1393—1396).—The iridotetrachloro-oxalates are intermediate between the iridichlorides and the iridodichloro-oxalates previously described (Abstr., 1909, i, 762). The *sodium* salt, $Na_3IrCl_4(C_2O_4)_2$, was obtained in solution by heating sodium oxalate with aqueous sodium iridichloride. The *potassium* salt obtained from this by double decomposition crystallises with $1H_2O$ in dark reddish-brown, orthorhombic prisms showing strong dichroism and double refraction. An aqueous solution gives no reaction for chloride or oxalate, but with silver nitrate yields an insoluble *silver* salt. The *rubidium*, *caesium*, and *ammonium* salts crystallise with $1H_2O$, and appear to be isomorphous with the potassium salt.

Iridotetrachloro-oxalic acid, prepared from the silver salt, is crystalline, but very unstable. In solution it decomposes into oxalic acid and a new acid, $HIrCl_4$, which has not been isolated. The existence of a substance of this constitution is assumed from the fact that the corresponding *barium* salt gives no silver chloride when treated with silver nitrate, but forms a green precipitate of the *silver* salt.

W. O. W.

New Types of Irido-oxalic Acids and Irido-oxalates. ALEXIS DUFFOUR (*Compt. rend.*, 1911, **152**, 1591—1594. Compare preceding abstract).—Gialdini's irido-oxalic acid (Abstr., 1907, i, 1005) is best prepared by the action of hydrochloric acid on the silver salt. When freshly prepared, its aqueous solution is golden-yellow, but on exposure to air becomes brown, and, finally, emerald-green. The solution now contains a new acid arising from the elimination of a molecule of oxalic acid from the original substance. The corresponding *potassium* salt, $KIr(C_2O_4),5H_2O$, obtained by adding potassium hydroxide (1 mol.), occurs in highly refractive, dichroic, green crystals, which lose $3H_2O$ at 110° without changing colour. On further treatment with potassium hydroxide (1 mol.), it forms an orange-red salt, $K_2[Ir(C_2O_4)_2(OH)(H_2O)],2H_2O$. The corresponding *acid*,

$$H_2[Ir(C_2O_4)_2(OH)(H_2O)],5H_2O,$$

forms monoclinic crystals, losing $3H_2O$ over sulphuric acid and $5H_2O$ at 110°; on treatment with potassium hydroxide (1 mol.), yellow dichroic prisms of the salt, $KH[Ir(C_2O_4)_2(OH)(H_2O)],2H_2O$, are obtained isomeric with the first-mentioned green salt, from which it can also be prepared by the action of heat on the aqueous solution.

W. O. W.

Action of the Oxides of Lead on Potassium Tartrate. FRANCIS C. KRAUSKOPF (*J. Amer. Chem. Soc.*, 1911, **33**, 943—947).—The solubility of litharge in solutions of alkali tartrates (Kahlenberg and Hillyer, Abstr., 1894, i, 275; Kahlenberg, Abstr., 1896, ii, 6) and the supposed insolubility of red lead and lead dioxide in such solutions indicated a method for freeing red lead and lead dioxide from litharge and for estimating the amount of litharge in samples of these oxides. It has been found, however, that both red lead and lead dioxide are soluble to some extent in alkali tartrate solutions.

A study of the action of red lead and lead dioxide on potassium tartrate solutions has shown that these oxides dissolve without causing the evolution of oxygen. In the case of lead dioxide, the tartrate is oxidised and lead carbonate is precipitated, but red lead dissolves without appreciable oxidation of the tartrate. The rotatory power of potassium tartrate solution is diminished by the addition of either litharge or red lead. Red lead causes a slightly greater diminution of the rotation than an equivalent quantity of litharge, and it is therefore evident that red lead is not reduced to litharge before dissolving. E. G.

Dibasic Ketonic Acids. EDMOND E. BLAISE and HENRI GAULT (*Bull. Soc. chim.*, 1911, [iv], **9**, 451—458, 458—464).—A more detailed account is given of the general method for the preparation of dibasic ketonic acids described already (Abstr., 1908, i, 713; 1909, i, 134, 362; 1910, i, 487, 542), and syntheses of new acids of this type are described. Ethyl oxalylsuccinate, b. p. 170—175°/12—13 mm., is a pale yellow oil which must be distilled rapidly in order to avoid much decomposition. Wislicenus and Nassauer's ester was probably chiefly ethyl ethanetricarboxylate (Abstr., 1895, i, 506). On condensation with propyl iodide, ethyl oxalylsuccinate gives ethyl *O-propyloxalylsuccinate*, $\frac{OPr^{\alpha}}{CO_2Et}{>}C{:}C{<}\frac{CO_2Et}{CH_2{\cdot}CO_2Et}$, b. p. 195—198°/15 mm. or 190—191°/13 mm. (Abstr., 1908, i, 713). On hydrolysis by hydrobromic or hydrochloric acid, this yields as one product (*loc. cit.*) α-ketoglutaric acid, $CO_2H{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, which gives a yellowish-green coloration with ferric chloride and furnishes a *phenylhydrazone*, m. p. 260° (approx. decomp.), separating from dilute alcohol in small, yellow crystals; and a *semicarbazone*, m. p. 220° (approx.), crystallising from warm water. Its reaction with hydrazine hydrate has been described by Gabriel (Abstr., 1909, i, 259). *Ethyl α-ketoglutarate*, b. p. 144°/13 mm., obtained by esterification of the acid in a closed tube at 120°, is a colourless liquid; the *semicarbazone*, m. p. 114°, is crystalline. Attempts to prepare the acid anhydride were unsuccessful.

Ethyl α-oxalyl β-methylsuccinate (Abstr., 1908, i, 713) furnishes a crystalline p-*nitrophenylhydrazone*. On heating, the ester furnishes *propane α-ββ-tricarboxylic acid*, m. p. 170° (decomp.), which on further heating yields methylsuccinic acid. On hydrolysis by acids, ethyl methyloxalylsuccinate furnishes *γ-keto-α′-methylglutaric acid*,

$$CO_2H{\cdot}CO{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H,$$

as a viscous liquid which is not volatile without decomposition. It yields an unstable *oxime*, m. p. 162° (approx.), a *semicarbazone*, m. p. 141—142°, a *phenylhydrazone*, m. p. 171—172°, and p-*nitrophenylhydrazone*, m. p. 163°, all of which are crystalline. The acid cannot be regenerated from the semicarbazone; the phenylhydrazone on dehydration, by heating at 140°, furnishes 1-*phenyl*-5-*methylpyridazin*-6-*one*-3-*carboxylic acid*, m. p. 134°, crystallising from water in lamellæ. By the direct action of hydrazine hydrate on methyl ketoglutaric acid, 5-*methylpyridazin*-6-*one*-3-*carboxylic acid*, m. p. 175°, is obtained.

Ethyl ketomethylglutarate, b. p. 144—145°/15 mm., obtained by

esterifying the acid in the usual way, is a colourless liquid; it forms a crystalline *additive product* with sodium hydrogen sulphite, and yields a *semicarbazone*, m. p. 98°, and a p-*nitrophenylhydrazone*, m. p. 109—110°, both of which are crystalline. T. A. H.

Ethyl Formylglutaconate and its Isomerides. WILHELM WISLICENUS and MARGARITA VON WRANGELL (*Annalen*, 1911, 381, 367—384. Compare Wislicenus and Bindemann, Abstr., 1901, i, 361).—The oily product formed by leaving ethyl formylglutaconate dissolved in moist ether for two to three days is shown to be a polymeride, namely, $C_{20}H_{28}O_{10}$, of the original ester. It is characterised by its oily consistency and by the red coloration it gives with ferric chloride. Moisture is essential for its formation; in dry benzene solution the original ester is stable, and can be kept for months; with the dry solid in a desiccator at the ordinary temperature the transformation is extremely slow, but rise of temperature favours the change. Small amounts of acid, on the other hand, retard the transformation. With sodium ethoxide the polymeride yields an orange-yellow salt, but is not so reactive as the original ester, for example, it does not react with bromine, hydrogen bromide, phenylhydrazine, or benzoyl chloride. Its *copper* derivative forms a deep green, slimy mass, which was obtained as a solid, m. p. 97°, on one occasion only. The structure suggested for the oily polymeric form is

$CO_2Et\cdot CH_2\cdot CH\dot{:}C(CO_2Et)\cdot CH(OH)\cdot CH(CO_2Et)\cdot CH\dot{:}C(CO_2Et)\cdot CHO$,

and this formula is in agreement with the fact that when heated at 120° under slight pressure the oil yields ethyl trimesate, formic acid, and ethyl acetate, and also with the formation of an additive compound, $C_{27}H_{33}O_{11}N$, with phenylcarbimide. It is probably that the original ester is first transformed into the tautomeric aldo-form before polymerisation occurs.

The *benzoyl* derivative of ethyl formylglutaconate,

$$CO_2Et\cdot CH\dot{:}CH\cdot C(CO_2Et)\dot{:}CH\cdot O\cdot COPh,$$

crystallises from ether in colourless needles, m. p. 63·5°, and the corresponding p-*nitrobenzoyl* derivative, $C_{17}H_{17}O_8N$, in colourless needles, m. p. 117°.

The *phenylcarbimide* additive product, $C_{17}H_{19}O_6N$, forms colourless plates, m. p. 74°. When bromine is added to its chloroform solution, the ester yields a *dibromide*, $C_{10}H_{14}O_5Br_2$, as an oil which does not react with ferric chloride. When distilled under 14 mm. pressure, it loses hydrogen bromide and yields an oily *ethyl bromoformylglutaconate*. $CO_2Et\cdot C(\dot{:}CH\cdot OH)\cdot CH\dot{:}CBr\cdot CO_2Et$, which gives an intense red coloration with ferric chloride. Potassium ethoxide transforms the oily bromo-ester into an *isomeric* solid, which crystallises from ether in colourless needles, m. p. 55—56°, and gives a violet coloration with ferric chloride. The *copper* derivative, $(C_{10}H_{12}O_5Br)_2Cu$, crystallises from benzene in small prisms, m. p. 144—145°.

Ethyl bromocoumalate, $CO_2Et<\genfrac{}{}{0pt}{}{CH—O}{CH\dot{:}CBr}>CO$, obtained by distilling ethyl bromoformylglutaconate, crystallises from alcohol in colourless prisms, m. p. 94—95°, and on hydrolysis with the theoretical

amount of potassium hydroxide solution yields Feist's furan-2 : 4-dicarboxylic acid (Abstr., 1901, i, 557).

Ethyl formylglutaconate dichloride forms a colourless oil, and when distilled under reduced pressure yields ethyl dichlorodihydrocoumalate, $CO_2Et\cdot C\begin{matrix}\nearrow CH\text{———}O\searrow \\ \searrow CHCl\cdot CHCl\nearrow\end{matrix}CO$, as an oil with b. p. 175—180°/18—20 mm. J. J. S.

Tetrolaldehyde (Δ^{α}-Butinal). PAUL L. VIGUIER (*Compt. rend.*, 1911, **152**, 1490—1493. Compare Abstr., 1909, i, 691).—Diethoxybutinene is best prepared by the action of ethyl orthoformate on magnesium allylene bromide. When the acetal is hydrolysed with 10% aqueous oxalic acid, *tetrolaldehyde*, CMe⋮C·CHO, is produced, and may be isolated by distillation in steam and extraction with ether. This substance is a colourless, mobile liquid with an intensely irritating odour, m. p. −26°, b. p. 27—28°/34 mm., 106·5—107° under ordinary pressure, D^{0} 0·944, D^{17} 0·9265, n_D^{17} 1·4467. It shows the usual reactions of an aldehyde and forms a very soluble compound with sodium hydrogen sulphite. The *semicarbazone* has m. p. 158°. The *oxime* crystallises in long needles, subliming at about 100°, m. p. 108—109°; at the ordinary temperature it changes slowly into methyl*iso*oxazolone (compare Claisen, this vol., i, 491).

Tetrolaldehyde reacts with hydrazine hydrate to give a *hydrazone*, b. p. 63—65°/15 mm., $D^{18\cdot5}$ 0·9768, $n_D^{18\cdot5}$ 1·530; the corresponding *azine* forms yellow needles, m. p. 123—124°. The hydrazone unites with phenylthiocarbimide, producing a *phenylthiosemicarbazone*, m. p. 114—116° (decomp.). 5-Methylpyrazole is formed when the aldehyde is heated with potassium hydroxide. W. O. W.

The Pinacolin Transformation. I. J. LINDNER (*Monatsh.*, 1911, **32**, 403—426).—The researches of previous investigators leave little doubt that pinacones and pinacolins have respectively the constitutions, for example, $OH\cdot CMe_2\cdot CMe_2\cdot OH$ and $CMe_3\cdot COMe$. During the conversion of the former into the latter by dilute acids, therefore, a methyl group has shifted from the one tertiary carbon atom to the other. The author hopes to show that the change is explicable by Erlenmeyer's theory of the intermediate production of a *cyclo*propane derivative, despite Montagne's criticism (Abstr., 1905, i, 445, 524). A suggestion is advanced to counter Montagne's objection that in the conversion to 4 : 4′ : 4″ : 4‴-tetrachlorobenzopinacone into the corresponding pinacolin, the halogen atoms are still in the para-position, whereas by Erlenmeyer's theory they should be in the ortho- or meta-positions, to the tertiary carbon atom. A serious objection to Erlenmeyer's theory, however, is Lieben's statement (Abstr., 1905, i, 167) that the pinacolin transformation is possible only with (purely aliphatic) pinacones which contain the group ⁚CMe·OH. Attention is drawn to the mobility of aromatic groups in glycols; thus Thörner and Zincke have shown that acetophenonepinacone yields only the pinacolin, $CMePh_2\cdot COMe$ (compare also Tiffeneau, Abstr., 1907, i, 130). This mobility, which may be due to the unsaturated character of the aromatic nucleus and its consequent ability to enter into ring formation, is in

favour of Erlenmeyer's theory. The theory would be proved by the isolation of the intermediately formed *cyclo*propanol derivative, for example, $OH{\cdot}CMe<\genfrac{}{}{0pt}{}{CMe_2}{CH_2}$.

With this end in view the author has prepared the two methyl ethers of acetonepinacone. An intimate mixture of the pinacone (1 mol.) and sodium is carefully warmed, and the resulting sodium derivative is heated for several days with methyl iodide. The separation of the two ethers is very difficult. The *methyl ether*, $OMe{\cdot}CMe_2{\cdot}CMe_2{\cdot}OH$, has b. p. 148—149°; the *dimethyl ether* has b. p. 144°; both are colourless liquids, with a pleasant odour recalling that of the pinacone.

A preliminary experiment with boric anhydride having shown that acetonepinacone can be thereby transformed into the pinacolin, the two ethers have been separately heated at 140° with this oxide, but in both cases the pinacolin, not the desired *cyclo*propanol derivative, is formed. The methyl ether is recovered unchanged after being heated with sodium acetate at 120—140°, or with barium oxide at 200°, but is partly converted into the pinacolin after being shaken with 25% sulphuric acid and kept for two weeks. The *acetate*, $OMe{\cdot}CMe_2{\cdot}CMe_2{\cdot}OAc$, b. p. 179—180°, of the methyl ether, obtained by the action of acetic anhydride and 3 drops of concentrated sulphuric acid for twelve days, has also been heated with boric anhydride at 110°, but methyl acetate and pinacolin are the only products which have been identified.

Dimethyl*iso*propylcarbinol, which is most conveniently prepared from methyl *iso*propyl ketone and magnesium methyl iodide, has also been examined in the hope that it might yield a *cyclo*propane derivative, $CMe_2<\genfrac{}{}{0pt}{}{CHMe}{CH_2}$, under the influence of acids. However, 20% sulphuric acid at 120° converts it almost quantitatively into $\beta\gamma$-dimethyl Δ^{β}-butylene, whilst the action of boric anhydride, which is different, has not yet been fully examined. The preceding experiments, although not fulfilling the author's hopes, indicate that the formation of esters plays an important part in the pinacolin transformation, which is a specific action of acids. C. S.

Ethyl Derivatives of Acetone. ERNST ZERNER (*Compt. rend.*, 1911, 152, 1599—1601).—Using Haller and Bauer's method (Abstr., 1910, i, 219—300), the author has prepared the tri-, tetra-, penta-, and hexa-ethyl derivatives of acetone.

$\gamma\gamma\epsilon$-*Triethylheptan-δ-one*, $CEt_3{\cdot}CO{\cdot}CHEt_2$, has b. p. 237·5—238·5°/761 mm. $\gamma\gamma\epsilon\epsilon$-*Tetraethylheptan-$\delta$-one*, $CEt_3{\cdot}CO{\cdot}CEt_3$, m. p. 44°, b. p. 274—275°/759 mm., has an apple-like odour, and does not undergo the usual scission when treated with sodamide. W. O. W.

Action of Hydrogen Peroxide on α-Diketones. JACOB BÖESEKEN, (Mlle.) LICHTENBELT, MILO, and VAN MARLEN (*Rec. trav. chim.*, 1911, 30, 142—147).—The normal course of the oxidation of α-ketonic acids, such as pyruvic, phenylglyoxylic, p-chlorophenylglyoxylic, and thienyl-

glyoxylic acids, by hydrogen peroxide results in the elimination of the ketonic group. The presence of a methyl group near the ketonic group, however, induces by-reactions; thus trimethylpyruvic acid is partly converted into *iso*butyric acid, and 2 : 4 : 6-trimethylphenylglyoxylic acid into phthalic acid.

Diacetyl is oxidised by hydrogen peroxide, yielding acetic acid, but not carbon dioxide; oxalic acid is only slowly and partly oxidised, yielding carbon dioxide, whilst oxamide, oxanilide, and oxanilic acid are almost unattacked, showing that the hydroxyl group largely, and the amino-group almost entirely, prevents the oxidation of the α-diketones.

β-Naphthaquinone is oxidised by hydrogen peroxide, yielding an unsaturated dibasic acid, m. p. 173—175° (*o*-carboxycinnamic acid?), whilst stearoxylic acid is quantitatively converted into azelaic and pelargonic acids; the latter oxidation furnishes another proof of the constitution of oleic acid. C. S.

The Destruction of Dextrose by Light. ADOLF JOLLES (*Biochem. Zeitsch.*, 1911, **33**, 252. Compare Mayer, this vol., i, 423).—The author reiterates his statement, that in alkaline solutions of dextrose when kept, the polarisation sinks to zero. The reaction must be carried out in well-closed flasks. S. B. S.

Action of Ultra-violet Light on Sucrose. HENRI BIERRY, VICTOR HENRI, and ALBERT RANC (*Compt. rend.*, 1911, **152**, 1629—1632. Compare Abstr., 1910, i, 625; this vol., i, 255).—The first action on sucrose of the light from a quartz-mercury lamp is to hydrolyse the sugar, and then to effect profound decomposition of the two hexoses, leading ultimately to the formation of formaldehyde and carbon monoxide. W. O. W.

Inversion of Sucrose in Ultra-violet Radiation. HANS VON EULER and H. OHLSÉN (*J. Chim. Phys.*, 1911, **9**, 416—422).—Aqueous solutions of sucrose were exposed in a quartz cell to the radiation from a quartz-mercury lamp. The solutions became heated to about 79° in twenty minutes, and were maintained at that temperature. The rate of hydrolysis appeared to be independent of the quantity of sugar present, and did not follow the unimolecular law. An acidic substance was progressively formed in the solutions, and the inversion was not greater than could be attributed to the action of this acid.
R. J. C.

Action of Alkalis on Chloraloses. MAURICE HANRIOT and ANDRÉ KLING (*Compt. rend.*, 1911, **152**, 1398—1399. Compare Abstr., 1910, i, 95).—Chloralose suffers decomposition when treated with aqueous alkalis, but if heated in sealed tubes with ammonia and methyl alcohol, it forms a *dichloro*-derivative, $C_7H_{11}O_6\cdot CHCl_2$, needles, m. p. 156—157°; the *tribenzoyl* derivative of this substance crystallises in needles, m. p. 192°. On hydrolysis, it yields dichloroacetaldehyde and dextrose, whilst nitric acid oxidises it to an *amide*, $C_7H_9O_5Cl_2\cdot CO\cdot NH_2$, m. p. 161—162°. The corresponding *acid* is

obtained in needles, m. p. 129—130°, by treating this with nitrous acid; it very readily forms a *lactone*, from which well defined salts are prepared by the action of alkalis. W. O. W.

Action of Ammonia on Chloraloses. MAURICE HANRIOT and ANDRÉ KLING (*Compt. rend.*, 1911, **152**, 1596—1599. Compare preceding abstract).—The reaction previously described is general for chloraloses. Ammonia withdraws an atom of chlorine from α-chloralose, replacing it by hydrogen, forming a *compound*, $C_8H_{12}O_6Cl_2$, long needles, m. p. 165°, in aqueous solution $[\alpha]_D +9·96°$; the *dibenzoyl* derivative has m. p. 146°. When the substance is treated with nitric acid, it forms a vitreous, feebly acidic *lactone*.

Galactochloralose and ammonia yield a *compound* isomeric with the foregoing, but existing in two modifications; one separates from water in crystals, m. p. 96°, but is changed in the second modification, m. p. 133°, on crystallisation from chloroform. The *dibenzoyl* derivative has m. p. 116°. Nitric acid oxidises the compound to mucic acid, whilst hydrochloric acid converts it into dichloroacetaldehyde and probably galactose.

The *compound*, $C_7H_{10}O_5Cl_2$, obtained from arabinochloralose has m. p. 88—89°, $[\alpha]_D -19·72°$; the *dibenzoyl* derivative has m. p. 90·5°. Nitric acid converts it into an *acid*, $C_7H_8O_6Cl_2$, m. p. 215°, and possibly this is accompanied by trihydroxyglutaric acid.

W. O. W.

An Experiment to Demonstrate the Reducing Properties of Cellulose. ROLAND SCHOLL (*Ber.*, 1911, **44**, 1312—1314. Compare Scholl and Berblinger, Abstr., 1904, i, 110; Scholl, *ibid.*, 1907, i, 540).—A simple experiment which demonstrates the reducing properties of cellulose in a few minutes is as follows: The specimen to be tested is digested for a few seconds with a dilute solution obtained by boiling flavanthren with water, dilute sodium hydroxide solution, and solid sodium hyposulphite. After washing, the yellow dye is developed by exposing the fabric to the air for a few minutes, or by treatment with hypochlorite solution. By heating the yellow fabric to boiling with a 2*N*-sodium hydroxide solution, the blue colour is restored. The length of time required for the reduction depends upon the amount of hydrocelluloses and oxycelluloses present in the original specimen. Oxycelluloses give an immediate blue colour, but when the oxycelluloses are removed by previous boiling with dilute sodium hydroxide solution, a longer time is required for the development of the blue colour, and the alkaline extract produces the coloration more rapidly than does pure alkali. Other vat dyes, such as pyranthrones or anthraquinoneazine, can be used in place of flavanthren. In the ordinary process of printing without specific reducing agents, the reduction is brought about by the dextrin, gum, etc., used. J. J. S.

Partial Hydrolysis of Tunicate Cellulose. Formation of Cellobiose. EMIL ABDERHALDEN and GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1911, **72**, 58—62).—The mere obtaining of dextrose from tunicin, the cellulose of tunicate animals, does not establish its identity

with vegetable cellulose. Further proofs of the identity or close relationship are now adduced, namely: (1) by the action of acetic anhydride in the presence of sulphuric acid, an acetyl compound (octa-acetylcellobiose) was obtained with the same melting point, solubility, composition, and optical activity as the product similarly obtained from filter paper; (2) the osazones of the cellobioses are also identical; (3) by saponification of the acetyl compound by means of barium hydroxide in the cold, crystallised cellobiose was obtained.

W. D. H.

Phosphates of Uranyl and of Amines. LÉONCE BARTHE (*Compt. rend.*, 1911, **152**, 1396—1397).—Double phosphates of the type $B'HUO_2PO_4$ have been prepared by saturating an aqueous solution of phosphoric acid with an amine, and adding a solution of uranyl acetate drop by drop. The compounds are precipitated in a pale yellow colloidal condition, and when dried in a vacuum become horny. They are very stable, and are not decomposed at 100°.

Methylamine uranyl phosphate, $NH_3Me\cdot UO_2PO_4$, has been obtained in this way, and also the corresponding *ethylamine* and *trimethylamine* salts.

W. O. W.

Preparation of Tetramethylenediamine [$\alpha\delta$-Diaminobutane]. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 232072).—A method for the technical preparation of $\alpha\delta$-diaminobutane has not previously been known; it is now found that a satisfactory yield can be obtained by treating adipodiamide, $NH_2\cdot CO\cdot[CH_2]_4\cdot CO\cdot NH_2$, with a halogen in aqueous alkaline solution; the amide dissolves, and the temperature rises to 70°; the reaction is completed by heating on the water-bath.

F. M. G. M.

Syntheses of Polypeptides. Derivatives of α-Aminobutyric Acid and their Behaviour towards Peptolytic Ferments. EMIL ABDERHALDEN, HSING LANG CHANG, and ERICH WURM (*Zeitsch. physiol. Chem.*, 1911, **72**, 24—36).—dl-α-*Formylaminobutyric acid*, $CH_2Me\cdot CH(CO_2H)\cdot NH\cdot CHO$, obtained by the action of formic acid on α-aminobutyric acid, crystallises from water in colourless plates, m. p. 153°, and can be resolved into its optically active components by means of brucine. The brucine salt, which is less soluble, is that of formyl-*l*-aminobutyric acid, although the formyl acid is dextrorotatory. On crystallisation the m. p. of the acid falls, probably owing to the removal of the formyl group.

When *dl*-α-aminobutyric acid is fermented with yeast in the presence of sucrose, the *d*-acid is destroyed before the *l*-acid, so that the product isolated by Fischer's esterification method is lævorotatory.

The action of active yeast extract on the three dipeptides, glycyl-*d*-aminobutyric acid and the corresponding *l*- and *dl*-compounds, has been investigated. The *l*-compound is not affected, but both the *d*- and *dl*-compounds are attacked.

From these results the conclusion is drawn that the α-aminobutyric acid which occurs in nature is the *d*-acid, as almost invariably it is the naturally-occurring acid which is more readily attacked by ferments.

Chloroacetyl-dl-α-*aminobutyric acid*, $CH_2Cl\cdot CO\cdot NH\cdot CHEt\cdot CO_2H$,

crystallises from ethyl acetate and light petroleum in pointed plates, m. p. 130° (corr.), and $[\alpha]_D^{20}$ $-18{\cdot}14°$. The corresponding *d*-compound has m. p. 119° (corr.) after sintering at 112°. *Glycyl*-dl-*α-aminobutyric acid*, $NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CHEt{\cdot}CO_2H$, crystallises from dilute alcohol in pointed needles, m. p. 231° (corr.), and the corresponding d-*acid* forms long needles, m. p. 223° (corr.), and has $[\alpha]_D^{20}$ $-12{\cdot}24°$.

Glycyl-l-*α-aminobutyric acid* has m. p. 222° (corr.) and $[\alpha]_D^{20}$ $+18{\cdot}29°$.

l-Alanine is best prepared from *d*-alanine from silk. The *d*-alanine is transformed into *l*-α-bromopropionic acid, and this on treatment with 10% aqueous ammonia at the ordinary temperature yields an alanine with $[\alpha]_D^{20}$ $-10{\cdot}3°$ (in form of the hydrochloride). J. J. S.

The Walden Inversion. VI. β-Aminobutyric Acid. EMIL FISCHER and HELMUTH SCHEIBLER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1911 566—586. Compare Abstr., 1910, i, 622).—β-Aminobutyric acid has been resolved into the optically active components by the crystallisation of the camphorsulphonate of its methyl ester. The active amino-acid may be converted into hydroxy-acid by means of nitrous acid or by treatment with nitrosyl chloride and subsequent boiling of the chlorobutyric acid formed with water. The two methods result in the formation of optically opposed hydroxy-acids, although the reactions are not so simple as with the α-amino-acids. In at least one of them a Walden inversion takes place, and this phenomenon is therefore extended to the β-series.

dl-Aminobutyric acid is prepared in quantity by heating crotonic acid with ammonia in an autoclave for twenty-four hours at 130—140°. The *methyl* ester, prepared by esterification with methyl alcohol and hydrogen chloride and decomposition of the hydrochloride so formed with ammonia, is a colourless, odorous liquid, b. p. 54—55°/13 mm., D^{20} 0·993.

dl-β-Aminobutyric acid has m. p. 191—192° (corr.). The copper salt is best prepared by repeated evaporation with copper acetate.

β-Naphthalenesulphonyl-dl-*β-aminobutyric acid*,

$$C_{10}H_7{\cdot}SO_2{\cdot}NH{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H,$$

crystallises in prisms, which sinter at 163°, m. p. 166—167° (corr.). *Methyl-β-iminodibutyrate* has b. p. 135°/12 mm., 144—145°/17 mm., D^{20} 1·044.

l-*β-Aminobutyric acid* crystallises in well-formed, thick prisms, decomp. about 220°, $[\alpha]_D^{20}$ $-35{\cdot}2°$ ($\pm 0{\cdot}2°$); the d-*isomeride* is very similar, $[\alpha]_D^{20}$ $+35{\cdot}3°$ ($\pm 0{\cdot}2°$); in *N*-hydrochloric acid it has $[\alpha]_D^{20}$ $+29{\cdot}7°$; in *N*-sodium hydroxide, $[\alpha]_D^{20}$ $+14{\cdot}7°$.

By the action of nitrous acid on *l*-β-aminobutyric acid, *d*-β-hydroxybutyric acid is obtained, the product being about 62% racemised. Nitrous acid acts in the same way optically on the methyl ester, methyl-*d*-β-hydroxybutyrate being formed.

By the action of nitrosyl chloride on *d*-β-aminobutyric acid, *l*-β-chlorobutyric acid is obtained, but little racemisation taking place.

d-β-Chlorobutyric acid crystallises in large prisms, m. p. 43—44·5°, $[\alpha]_D$ $+49{\cdot}8°$ ($\pm 0{\cdot}2°$). E. F. A.

Methylated Polypeptides. EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1911, 72, 44—49).—*Trimethylleucylglycine*, $CHMe_2{\cdot}CH_2{\cdot}CH(NMe_3{\cdot}OH){\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$ or $CHMe_2{\cdot}CH_2{\cdot}CH{<}\begin{matrix}CO{\cdot}NH{\cdot}CH_2\\ NMe_3\text{———}O\end{matrix}{>}CO$, may be obtained by methylating *dl*-leucylglycine with methyl iodide in the presence of methyl alcohol and *N*-potassium hydroxide at the ordinary temperature, and is best isolated as the *platinichloride*, $(C_{11}H_{23}O_3N_2)_2PtCl_6$, which crystallises from water in brilliant orange-red prisms or plates. The *aurichloride*, $C_{11}H_{23}O_3N_2AuCl_4$, also crystallises from water in orange-yellow prisms, m. p. 170—172°, after softening at a lower temperature. The *picrate* crystallises from dilute alcohol in brilliant lemon-yellow prisms, m. p. 228—229° (corr.), and decomposing at 240—250°. J. J. S.

Salts and Esters of Alkylaminodithiocarbamic Acids. ERNEST FOURNEAU (*Bull. Soc. chim.*, 1911, [iv], 9, 532—536).—Methylaminoacetic acid reacts in ether with carbon disulphide to form the corresponding *dithiocarbamate*,

$$CO_2Et{\cdot}CH_2{\cdot}NMe{\cdot}CS{\cdot}S{\cdot}NH_2Me{\cdot}CH_2{\cdot}CO_2Et,$$

m. p. 77°, which crystallises in colourless, inodorous, hexagonal tablets, and is very soluble in alcohol or water. On adding mercuric chloride to the aqueous solution, the *mercury* derivative,

$$(CO_2Et{\cdot}CH_2{\cdot}NMe{\cdot}CS_2)_2Hg,$$

m. p. 148°, is formed. It crystallises from boiling alcohol in slender, yellow needles, and is soluble in acetone. The corresponding *mercury* derivative of the *propyl* ester, $(CO_2Pr^a{\cdot}CH_2{\cdot}NMe{\cdot}CS_2)_2Hg$, m. p. 86°, resembles its lower homologue. On adding sodium hydroxide to an alcoholic solution of either of these substances, the unstable *compound*, $(CO_2Na{\cdot}CH_2{\cdot}NMe{\cdot}CS_2)_2Hg$, is precipitated in the form of small, colourless needles.

Similar series of derivatives are formed from the ethyl esters of ethylaminoacetic and methylaminohydroxy*iso*butyric acids, whilst ethyl phenylmethylaminoacetate reacts with carbon disulphide to form the *dithiazolone*, $\begin{matrix}Ph\\ R\end{matrix}{>}C{<}\begin{matrix}NMe{\cdot}CS\\ CO\text{——}S\end{matrix}$. T. A. H.

Derivatives of *s*-Diaminoacetone. ANTOINE P. N. FRANCHIMONT and J. V. DUBSKY (*Rec. trav. chim.*, 1911, 30, 177—182).—The reaction of *s*-diaminoacetone hydrochloride with ethyl chloroformate under the conditions employed by Franchimont and Friedmann (Abstr., 1907, i, 832) yields *ethyl acetone-αγ-diurethane*,

$$CO(CH_2{\cdot}NH{\cdot}CO_2Et)_2,$$

m. p. 136—137°. This substance is not attacked by boiling acetic anhydride alone, but in the presence of a little zinc chloride yields the *diacetyl* derivative, $CO(CH_2{\cdot}NAc{\cdot}CO_2Et)_2$, m. p. 61—62°. It nitrates readily, forming the *αγ-dinitro*-compound, $C_9H_{14}O_9N_4$, m. p. 56—57°.

Tetra-acetyl-1 : 3-*diaminoacetone*, $CO(CH_2{\cdot}NAc_2)_2$, obtained by boiling 1 : 3-diacetylaminoacetone (*loc. cit.*) for three hours with a large excess of acetic anhydride, forms large needles, which soften at 98°, and have m. p. 108°. C. S.

A Tetra-acetyl Aminoglucoside. MARSTON L. HAMLIN (*J. Amer. Chem. Soc.*, 1911, **33**, 766—769).—The work described in this paper has been forestalled by the publication of Irvine, McNicoll, and Hynd's paper on new derivatives of *d*-glucosamine (Trans., 1911, **99**, 250). These authors' results are confirmed, but it is found that bromotriacetylglucosamine hydrobromide does not melt, but darkens at 138—148°, and chars at 153° (uncorr.).

When a solution of bromotriacetylglucosamine hydrobromide in methyl alcohol is shaken with silver carbonate and filtered, the filtrate boiled with acetic anhydride, the methyl alcohol and acetic anhydride removed by distillation in a vacuum, and the residue boiled with a further quantity of acetic anhydride, *tetra-acetylglucosamine methylglucoside*,

$$OAc{\cdot}CH_2{\cdot}CH(OAc){\cdot}\overbrace{CH{\cdot}CH(OAc){\cdot}CH(NHAc){\cdot}CH}^{O}{\cdot}OMe,$$

m. p. 150·5° (uncorr.), is obtained, which forms a white, crystalline powder. This compound is not a derivative of the aminoglucoside prepared by Fischer and Zach (this vol., i, 117), since the latter on hydrolysis yields the hydrochloride of an amino-sugar which is not identical with glucosamine hydrochloride. E. G.

Preparation of Acetamide. MARTIN A. ROSANOFF, LOUISE GULICK, and HERBERT K. LARKIN (*J. Amer. Chem. Soc.*, 1911, **33**, 974—977).—Acetamide can be prepared in good yield by the following method.

Dry ammonium acetate is prepared by neutralising glacial acetic acid with powdered ammonium carbonate at about 50°, allowing the product to cool, draining the crystals, and pressing them between filter paper. A mixture of this ammonium acetate (1 mol.) and glacial acetic acid (1·5 mols.) is boiled for five hours under a reflux condenser. The product is rapidly distilled, and the distillate is submitted to slow fractional distillation, using a two-bulb Wurtz dephlegmator. Three fractions are collected : (1) below 180° ; (2) between 180° and 213°, and (3) above 213°. The second fraction is redistilled, and the portion passing over above 213° is added to fraction 1. The portion with high-boiling point, after it has solidified, is pressed between filter paper, and the dry crystals thus obtained consist of almost pure acetamide (b. p. 214—216°). The yield from 100 grams of ammonium acetate amounts to over 60 grams, or about twenty grams more than can be obtained by the Hoffmann-Gattermann method. The yield cannot be increased by carrying out the reaction in sealed tubes. E. G.

Acetylation of Substituted Acetamides. ANTOINE P. N. FRANCHIMONT and J. V. DUBSKY (*Rec. trav. chim.*, 1911, **30**, 183—185). —The formation of tetra-acetyldiaminoacetone (this vol., i, 528) is merely an instance of a general reaction, whereby mono- and di-substituted amines are acetylated by boiling with a large excess of acetic anhydride. Thus acetmethylamide is converted into diacetylethylamine, acetethylamide into diacetylethylamine, and *s*-diacetylethylenediamine into *tetra-acetylethylenediamine*, $NAc_2{\cdot}CH_2{\cdot}CH_2{\cdot}NAc_2$, m. p. 156—157°. C. S.

Ammonium Cyanate and Carbamide. RICHARD ESCALES (*Chem. Zeit.*, 1911, **35**, 595).—The author (with H. KÖPKE) has found that when carbamide is sublimed in a vacuum at 160—190°, the sublimate consists of ammonium cyanate. He remarks that if Wöhler had endeavoured to purify his synthetical urea by sublimation, his famous discovery might never have been made. L. DE K.

Catalytic Action of Ferric Thiocyanate. H. COLIN and A. SÉNÉCHAL (*Compt. rend.*, 1911, **152**, 1586—1587).—The authors consider that ferric thiocyanate is not strictly speaking a specific peroxydase. Its action in bringing about oxidation of phenols in presence of hydrogen peroxide is partly due to decomposition of the salt, whereby peroxy-acids of sulphur are formed. Potassium thiocyanate acts in the same way as the iron salt, but not to such a marked extent. W. O. W.

Aliphatic Nitro-compounds. X. Hydroxamyl Chlorides. WILHELM STEINKOPF and BORIS JÜRGENS (*J. pr. Chem.*, 1911, [ii], **83**, 453—470. Compare Abstr., 1910, i, 280).—The substance, previously recorded as β-oximino-oxalimino-chloride from its reactions and methods of formation, may be chloro-oximinoacetamide, produced, for example, from nitroacetonitrile and hydrogen chloride in dry ether, by the following series of reactions: $NO_2\cdot CH_2\cdot CN \xrightarrow{HCl}$ $NOH{:}C(OH)\cdot CN \longrightarrow NOH{:}CCl\cdot CN + H_2O \longrightarrow NOH{:}CCl\cdot CO\cdot NH_2$. At first sight the explanation appears improbable, because it is unlikely that the water formed in the second reaction can convert the nitrile into the amide in the presence of the large excess of ether. However, the discovery that hydrogen chloride converts ethyl nitroacetate in dry ether into ethyl chloro-oximinoacetate shows that the first two phases of the series above can occur. The fact that the third phase does occur, and that the so-called β-oximino-oxalimino-chloride is really chloro-oximinoacetamide, is proved by the action of aqueous sodium carbonate on the substance in the cold, whereby an odour of a nitrile oxide is observed, and furoxandicarboxylamide (dinitrosoperoxide of succinamide) is formed.

From analogy to the preceding, the so-called α-oximino-oxalimino-chloride, m. p. 173—174° (decomp.), produced from methazonic acid and hydrogen chloride in ether (*loc. cit.*), must be chloro-oximinoacetaldoxime (chloroglyoxime), $NOH{:}CCl\cdot CH{:}NOH$. This is so, because not only is the substance converted by thionyl chloride in dry ether into *chloro-oximinoacetonitrile*, $CN\cdot CCl{:}NOH$ (which is too unstable to be analysed, but yields with aniline, *anilino-oximinoacetonitrile*, $NHPh\cdot C(CN){:}NOH$, m. p. 138—139°), but also the identity of the substance with Hantzsch's chloro*anti*glyoxime, m. p. 161° (Abstr., 1892, 693) (the m. p. can be raised to 168° by repeated crystallisation), is proved by the fact that the two substances form the same acetyl derivative, m. p. 163—164°, and diacetyl derivative, m. p. 90·5°. Moreover, a moist ethereal solution of the chloro-oximinoacetonitrile is hydrolysed by hydrogen chloride, yielding chloro-oximinoacetamide. *Chloro-oximinoacetic acid*, $NOH{:}CCl\cdot CO_2H$, decomp. 129°, is obtained by keeping for three weeks a suspension of potassium

nitroacetate in dry ether saturated with hydrogen chloride in the cold.

In Nägeli's chloro*amphi*glyoxime (Abstr., 1883, 728) the chlorine atom and one of the hydroxyl groups have the *anti*-configuration, because the substance is insensitive to alkalis and does not yield a nitrile oxide with sodium carbonate. Now an aqueous solution of this *anti*chloro*amphi*glyoxime reacts with aniline to form a *salt*, NOH:CCl·CH:NOH,NH_2Ph, m. p. 114° (decomp.). This behaviour not only illustrates the stability of the halogen atom in *anti*hydroxamyl chlorides, but may also serve for the characterisation of such substances, because other hydroxamyl chlorides, in which the chlorine atom and the hydroxyl group have the *syn*-configuration, react with aniline to form anilino-derivatives by substitution of the halogen atom. The authors deduce from the preceding that the α- and the β-oximinohydroxamic acids previously described (*loc. cit.*) have the *anti*- and the *syn*-configurations respectively.

By chlorinating a cold solution of chloro*anti*glyoxime in dilute hydrochloric acid, anti*dichloroglyoxime* (*αβ-dichloro-αβ-dioximinoethane*), NOH:CCl·CCl:NOH, m. p. 201°, is obtained, which yields the odour of a nitrile oxide by heating or by treatment with sodium carbonate, forms a *dibenzoyl* derivative, m. p. 217°, and reacts with aniline to form αβ-dianilino-αβ-dioximinoethane.

Ethyl iodo-oximinoacetate, CO_2Et·CI:NOH, m. p. 95—96°; *iodo-oximinoacetamide*, NOH:CI·CO·NH_2, yellow crystals, decomp. 154—155°; *iodo*anti*glyoxime*, NOH:CI·CH:NOH, m. p. 136°, and anti*di-iodoglyoxime*, NOH:CI·CI:NOH, decomp. 172°, are obtained by heating the corresponding chloro-compounds with a solution of sodium iodide in acetone. *anti*Chloro*amphi*glyoxime does not react with sodium iodide in acetone, another instance of the stability of the chlorine atom in *anti*chloro-oximino-compounds. C. S.

Friedel and Crafts' Reaction. JACOB BÖESEKEN (*Rec. trav. chim.*, 1911, 30, 148—150).—The formation of *as*-heptachloropropane from tetrachloroethylene and chloroform in the presence of aluminium chloride (this vol., i, 173) is typical of the reactions between trichloroethylene and chloroform, trichloroethylene and carbon tetrachloride, dichloroethylene and chloroform, and dichloroethylene and carbon tetrachloride; in every case the initial reaction is the simple addition of the two molecules.

The preceding explains the nature of the Friedel and Crafts' reaction. Three molecules must be present: (*a*) an unsaturated molecule, (*b*) a molecule which can be so activated that it can combine with the unsaturated molecule, (*c*) a catalyst which activates the molecules in (*a*) and (*b*). The possibility of the reaction is determined by the loss of free energy. The initial action is due to the encounter of the two molecules with the catalyst; in the case of benzene and other unsaturated cyclic systems the initial additive product, a derivative of dihydrobenzene, etc., cannot be isolated, because by elimination of hydrogen chloride or the like it is converted into a system containing less free energy. C. S.

Friedel and Crafts' Reaction. XI. Action of Sulphur Monochloride on Benzene, Chlorobenzene, and Toluene. JACOB BÖESEKEN and D. A. WITTOP KONING (*Rec. trav. chim.*, 1911, **30**, 116—136).—The reaction between benzene and sulphur monochloride in the presence of aluminium chloride is more complex than that previously recorded (Abstr., 1905, i, 583), since diphenyl disulphide is always formed. The formation of the disulphide, if produced by a primary reaction, indicates that sulphur monochloride may have a symmetrical constitution.

The authors have examined quantitatively the action of sulphur monochloride on an excess of benzene, chlorobenzene, or toluene in the presence of an excess of aluminium chloride. When the reaction is completed, the sulphur monochloride has been entirely destroyed. Estimations are made of the sulphur present in the free state or combined as hydrogen sulphide, aromatic sulphide, aromatic disulphide, thianthren, or in the side-chain (in the case of toluene).

The reaction is simplest in the case of chlorobenzene; hydrogen sulphide and a thianthren are not formed, the products consisting of sulphur, di-*p*-chlorophenyl sulphide, and di-*p*-chlorophenyl disulphide (identified by oxidising it to chloronitrobenzenesulphonic acid by nitric acid, D 1·5). The reaction with benzene yields sulphur, hydrogen sulphide, diphenyl sulphide, diphenyl disulphide, thianthren, and a trace of phenyl mercaptan.

The reaction is still more complicated in the case of toluene; in addition to substances corresponding with the preceding, a small amount of dibenzyl sulphide (and disulphide?) is formed by substitution in the side-chain.

Despite these quantitative examinations, a clear picture of the reaction of sulphur monochloride and benzene (or chlorobenzene or toluene) cannot be drawn, because the primary reaction is obscured by secondary reactions due to the action, in the presence of the catalyst, of the liberated sulphur on the benzene and the diphenyl sulphide, and to the decomposition of the disulphide. C. S.

The System Propylbenzene–Antimony Trichloride. BORIS N. MENSCHUTKIN (*J. Chim. Phys.*, 1911, **9**, 314—322).—Propylbenzene, b. p. 157°/765 mm., becomes viscous on cooling, and solidifies below −100° to an isotropic mass, which has no definite melting point. When small proportions of antimony chloride are present, crystals of an additive compound separate on cooling. The compound usually has the formula $SbCl_3,C_6H_5Pr$, m. p. +1·5°, but sometimes consists of $2SbCl_3,C_6H_5Pr$, m. p. +9° to +10°, which is less soluble.

There are two distinct liquidus curves, representing the stable and labile compounds respectively. These curves cut the antimony trichloride liquidus at +1° and +8·5°, representing two distinct eutectics. The two liquidus curves are practically parallel, the difference being 8° near the eutectic points, and about 11° at 3% antimony trichloride concentration. The less fusible compound was not obtained spontaneously above 15% of antimony chloride, but could be easily obtained by sowing the more concentrated solutions.

According to the phase rule, the more soluble, more fusible com-

pound should be labile, whereas in the experiments the more fusible compound was the more readily obtainable. R. J. C.

Bromination of Some Hydroaromatic Compounds. FERNAND BODROUX and FELIX TABOURY (*Compt. rend.*, 1911, **152**, 1252—1254; *Bull. Soc. chim.*, 1911, [iv], **9**, 595—601).—*cyclo*Hexane is converted into an oily monobromo-derivative when treated with bromine in sunlight; further treatment with bromine changes this into 1 : 2-dibromo*cyclo*hexane. The bromination of *cyclo*hexane, menthene, and thymomenthene in presence of aluminium bromide leads to the production of viscous liquids. Dibromo*cyclo*hexane and *cyclo*hexene under the same conditions give hexabromobenzene. Methyl*cyclo*hexane and Δ^2- and Δ^4-methyl*cyclo*hexenes yield pentabromotoluene amongst other products. 1 : 3-Dimethyl*cyclo*hexane furnishes a mixture of isomeric tetrabromoxylenes. W. O. W.

Action of Sulphur on Aromatic Sulphones. JACOB BÖESEKEN (*Rec. trav. chim.*, 1911, **30**, 137—141).—When heated with rather more than 1 atom of sulphur at 250—275° in a current of dry carbon dioxide, the following sulphones do not yield sulphides, as does diphenylsulphone (Krafft and Vorster, Abstr., 1894, i, 88), but decompose in a characteristic manner. 4 : 4′-Dichlorodiphenylsulphone yields *p*-dichlorobenzene and sulphur dioxide; 4 : 4′-dibromodiphenylsulphone decomposes similarly, but less readily. 4-Chloro-4′-bromodiphenylsulphone yields *p*-chlorobromobenzene. 4-Bromophenyl-*p*-tolylsulphone yields hydrogen sulphide, water, hydrogen bromide, and a little red oil. C. S.

Action of Dichloromethane on Di-*p*-tolylmethane. JAMES LAVAUX (*Compt. rend.*, 1911, **152**, 1400—1402. Compare Abstr., 1905, i, 43, 125, 640, 698; 1906, i, 25; 1907, i, 150, 256).—To solve the problem of the constitution of the supposed 1 : 6- and 2 : 7-dimethylanthracenes previously obtained by the action of dichloromethane and aluminium chloride on a mixture of isomeric ditolylmethanes, the condensation has been repeated on a pure specimen of di-*p*-tolylmethane. The latter prepared by the action of trioxymethylene on toluene in presence of sulphuric acid, occurs in needles, m. p. 28° (Ador and Rillet give 22—23°; Weiler, below −15°). It was found, however, that the pure hydrocarbon gave the same mixture of dimethylanthracenes, indicating that aluminium chloride has brought about a transposition similar to that which it effects in converting *n*-propyl into *iso*propyl derivatives. W. O. W.

Hydrogenation by means of (1) Spongy Palladium and Sodium Hypophosphite, (2) Nickel and Sodium Hypophosphite. PIERRE BRETEAU (*Bull. Soc. chim.*, 1911, [iv], **9**, 515—517, 518—519. Compare this vol., i, 123).—Spongy palladium, precipitated from a solution of the chloride by sodium hypophosphite, decomposes water in presence of sodium hypophosphite, forming hydrogen and sodium hydrogen phosphite, and this mixture is useful as a reducing agent. In boiling alcohol, it reduces phenanthrene to the tetrahydride, and nitro- or dinitro-derivatives to the corresponding amines.

In the second paper it is shown that nickel in powder form, prepared by adding sodium hypophosphite to a hot solution of nickel sulphate, also decomposes water in presence of sodium hypophosphite. This mixture does not reduce phenanthrene, although it converts nitro-derivatives into the corresponding amines. T. A. H.

Compounds which Cause the Red Coloration of Aniline. II. Effect of Sunlight in the Absence of Oxygen and Oxidising Influences and a Comparison with the Behaviour of Mono- and Di-methylaniline. HARRY D. GIBBS (*Philippine J. Sci.*, 1910, 5, 419—435. Compare Abstr., 1910, i, 550).—Aniline purified by various processes is sealed in glass tubes either in a vacuum or in an atmosphere of hydrogen, and exposed to sunlight for many (51—60) days during the summer months. The liquid acquires a very deep red, almost black, colour. The products are azophenine, benzene, and ammonia. The rate of coloration appears to increase with the pressure of the hydrogen in the tube. Aniline in tubes containing carbon dioxide colours very much less rapidly, the rate of coloration being greatest when the pressure of the gas is least. Methylaniline in an atmosphere of hydrogen also becomes red in sunlight (methylamine is present among the products), whilst dimethylaniline is only slightly coloured, the coloration probably being due to impurities.

From these and the previous experiments on aniline (*loc. cit.*) and phenol (Abstr., 1909, i, 221, 640), it seems that the fixation of the labile hydrogen atom destroys the sensibility of the molecule to chemical change produced by sunlight. Attention is called to the fact that the introduction of methyl or ethyl groups into certain dyes to produce methyl or ethyl ethers, increases the fastness of the dye to light. C. S.

Mechanism of the Elimination of Halogens by Aromatic Amines. IWAN OSTROMISSLENSKY and PAWEL ALABÉEFF (*J. pr. Chem.*, 1911, [ii], 83, 506—512).—Hitherto an explanation has not been attempted of the fact that certain aromatic amines (aniline, phenylhydrazine, quinoline, pyridine) eliminate the halogen from various olefine dihalogenides with the regeneration of the original olefine. Thus the authors show that when stilbene dibromide is heated with dry pyridine for twelve hours on the water-bath, about 87% of the halogen is eliminated as hydrogen bromide, stilbene itself being formed. Consequently, in such reactions the hydrogen of the halogen acid must have been withdrawn from the aromatic amine, and, furthermore, must have been withdrawn from the aromatic nucleus, since the elimination in question can be effected by tertiary amines. It follows, therefore, that unstable groups, such as $\cdot C_6H_4\cdot NH_2$, must be formed. From these groups, by intramolecular change, polymerisation, etc., probably are formed the resinous substances which are almost invariably produced in the reactions in question. The formation of benzidine itself has never been observed in such reactions.

The authors' explanation accounts for the formation of tetramethyldiaminodiphenylethane observed by Schoop when dimethylaniline and ethylene dibromide are heated for eight days in the water-bath.

C. S.

Catalytic Hydrogenation of Cyclic Oximes. Synthesis of Arylamines. ALPHONSE MAILHE and MARCEL MURAT (*Bull. Soc. chim.*, 1911, [iv], 9, 464—468).—The reduction of aliphatic oximes to amines by means of finely divided metals has been described already (Abstr., 1905, i, 571, 635), and this work has now been extended to cyclic oximes. These are reduced less easily than the aliphatic oximes. The normal reaction is the formation of a mixture of the corresponding primary and secondary amines, the latter predominating, but in addition other reactions occur. The water formed leads to the regeneration of the parent ketone, and a part of the primary amine formed is decomposed, forming ammonia and olefinic hydrocarbons, the latter being in part reduced to the saturated hydrocarbons by the action of the metal; thus aminophenylbutane furnishes with hot, finely-divided nickel, ammonia, phenylbutylene, and phenylbutane. Except in the case of benzophenoneoxime this decomposition of the primary amine formed occurs to a large extent in all the cases tried.

The following new compounds were obtained: Acetophenoneoxime gave the *secondary amine*, $NH(CHMePh)_2$, b. p. 295—298° (approx.), D^{13} 1·018, n_D 1·573. Propiophenoneoxime gave the *secondary amine*, $NH(CHEtPh)_2$, b. p. 310—315°, the *hydrochloride* of which has m. p. 200° (approx. decomp.). Butyrophenoneoxime, m. p. 49°, b. p. 248°, furnished the *primary amine*, $CHPrPh \cdot NH_2$, b. p. 240°, D^{13} 0·9813, n_D 1·534, and a small quantity of *secondary amine*, b. p. 320° (approx.). Benzophenoneoxime gave a 70% yield of benzhydrylamine with some *dibenzhydrylamine*, m. p. 126°, the *hydrochloride* of which melts at 300° (approx. decomp.).

o-Methyl*cyclo*hexanoneoxime furnished the *primary amine*, b. p. 150°, and the *secondary amine*, b. p. 260° (approx. decomp.), the *hydrochloride* of which has m. p. 225° (approx. decomp.). The isomeric meta-*secondary amine* has b. p. 265° (decomp.), whilst the para-*secondary amine* has b. p. 265° (approx. decomp.).

Menthoneoxime yields *dimenthylamine*, b. p. 305°, the *hydrochloride* of which has m. p. 207° (approx. decomp.). T. A. H.

Quantitative Examination of the Introduction of One Atom of a Halogen into Phenol. ARNOLD F. HOLLEMAN and I. J. RINKES (*Rec. trav. chim.*, 1911, 30, 48—100).—The authors have plotted the freezing-point curve of mixtures of *o*- and *p*-bromophenol, using specially purified materials; the eutectic point is at $-11·7°$.

By brominating phenol with exactly the calculated amount (1 mol.) of bromine, either as vapour diluted with air or carbon dioxide or in a solvent, it is possible to conduct the operation quantitatively in such a way that no phenol remains unattacked and no dibrominated products are formed. After the bromination is complete and the solvent, if such has been used, has been removed by suitable methods (which are described), the product is distilled as completely as possible in a vacuum and the freezing point of the distillate is determined; reference to the freezing-point curve then gives the composition of the mixture, providing it consist only of *o*- and *p*-bromophenols. That the meta-isomeride is never produced is proved in the following way. The

brominated product is nitrated by nitric acid, D 1·52, at $-5°$, the resulting nitrated bromophenols are treated with methyl-alcoholic sodium methoxide (1 mol.), the alcoholic solution is added to water acidified with nitric acid after twenty minutes, the phenolic substances are removed by ether, and the aqueous solution is tested with silver nitrate; the absence of a precipitate of silver bromide proves that no halogen has been eliminated from the nitrated bromophenols by the sodium methoxide, and therefore that no *m*-bromophenol was originally present, since this is the only bromophenol which yields by nitration a product containing nitro-groups in the ortho- and para-positions to the bromine atom. A distinct turbidity of silver bromide was produced when a mixture of *o*- and *p*-bromophenols containing 1% of the meta-isomeride was examined by the preceding process.

The presence of only *o*- and *p*-bromophenols in the product of the bromination of phenol is also proved by adding to the product (the composition of which has been ascertained from its freezing point) the amount of *o*-bromophenol required to bring its composition to that of the eutectic mixture; the freezing point is then found to be that, or very nearly that, of the eutectic mixture, $-11·7°$.

The percentages of *p*-bromophenol obtained are as follows: 97·4% at $-30°$, 92·8% at 0°, 86·2% at 30°, with carbon disulphide as solvent; 91·2% at 15°, 87·5% at 30°, 86·8% at 60°, with glacial acetic acid as solvent; 88·6% at 30°, with carbon tetrachloride as solvent; 90·2% at 60°, 90·7% at 90°, 81·6% at 131°, 79·4% at 153°, and 77% at 180°, without a solvent. The increase with the temperature in the percentage of *o*-bromophenol is much less than might be expected from references in the literature; also, for example at 30°, the composition of the mixture apparently is almost independent of the nature of the solvent.

o-Bromophenol has been prepared by brominating phenol without a solvent at 170° and fractionating the product; in addition to the usual form, m. p. 5·5°, a second modification of *o*-bromophenol has been discovered which solidifies at $-10°$ (compare Ostromisslensky, Abstr., 1907, i, 120).

The chlorination of phenol without a solvent has been performed at 40°, 90°, and 155°, the percentages of *p*-chlorophenol, determined from the freezing-point curve of *o*- and *p*-chlorophenols, being 47·3, 50·2, and 48·8 respectively. It should be noted that the percentage of the para-isomeride is much less than that obtained by bromination, and remains nearly constant between 40° and 155°.

The quantitative conversion of phenol into iodophenols by direct iodination cannot be performed; even with a large excess of phenol the product contains unchanged substance and polyiodophenols. The main product, however, is *p*-iodophenol, the following method being very convenient for obtaining this substance. A solution of iodine in potassium iodide is added to an excess of aqueous phenol. Sodium hydroxide is added until the mixture is decolorised, and finally concentrated hydrochloric acid. The resulting oil is distilled at 76°/0·8 mm., whereby unchanged phenol is almost entirely removed. The residue is finally recrystallised from petroleum. C. S.

Dyeing with Picric Acid. GEORG VON GEORGIEVICS (*Monatsh*, 1911, 32, 319—327).—The rule that the presence of sulphuric or other acid is essential for the adsorption of an acid dye by the fibre does not hold for picric acid at concentrations between about 0·008 and 0·017%, for the author finds that the amount of picric acid adsorbed from aqueous solutions of these concentrations is almost the same when an amount of sulphuric acid approximately equal to that of the picric acid is added to the bath.

Walker and Appleyard (Trans., 1896, 69, 1334) have shown that the adsorption of picric acid by silk at 60° is such that the expression $C/\sqrt[2\cdot7]{C'}$ = constant, where C and C' are the concentrations of the dye in the fibre and in the bath respectively. The partition is independent of the temperature, the author's experiments at the ordinary temperature yielding the same result with the exception that the root exponent is 2·64 instead of 2·7. In the author's experiments the concentration of the picric acid varies from 0·02 to 0·4%. At the former concentration the value of the expression $C/\sqrt[2\cdot64]{C'}$ is very much below the mean value, a result which possibly may be due to the prolonged time requisite for equilibrium to be attained in very dilute solutions. The colour can be removed from the dyed silk by repeated treatment with acetone at the ordinary temperature.

The dyeing of animal fibres by acid dyes is often attributed to the formation of molecular compounds between the dye and the fibre. This explanation appears doubtful in the light of the following experiments. When the molecular compound naphthalene picrate is washed with water, the washings soon contain a constant amount, 0·08%, of picric acid; naphthalene, introduced into a solution of 0·08% picric acid, does not form any picrate. Silk containing 3% of picric acid is washed with water, and the washings contain about 0·003% of picric acid. If the dyeing of the silk is due to the formation of a molecular compound analogous to naphthalene picrate, it is to be expected that silk will not adsorb any dye from a 0·003% solution of picric acid; experiment shows, however, that at this or even smaller concentrations the silk removes almost the whole of the picric acid from the solution.

Experiments are described which seem to indicate that the darkening of picric acid by exposure to the air is due to salt formation (ammonium picrate?). Also the fact that wool, dyed by picric acid in the cold, acquires a deeper tone by boiling with water (Abstr., 1906, i, 420) may be due to the formation of picrates of the basic decomposition products of the wool. It is still unexplained, however, why aqueous solutions of picric acid darken by boiling, even in the presence of a little hydrochloric acid. C. S.

The Separation of *p*-Chloro-*m*-cresol ($CH_3:OH:Cl = 1:3:6$) from Mixtures of *m*- and *p*-Cresol. FRITZ RASCHIG (D.R.-P. 232071).—The action of sulphuryl chloride (or chlorine) on a cooled solution of the technical mixture of *m*- and *p*-cresols is selective; if only sufficient chlorine is introduced to react with the *m*-cresol this alone is attacked, and on subsequent distillation (at atmospheric pressure)

the *p*-cresol will pass over at 200°, followed at 235° by pure *p*-chloro-*m*-cresol. A certain amount of o-*chloro*-m-*cresol*, b. p. 196°/760 mm., is also formed, and passes over with the *p*-cresol, from which it is subsequently separated; it is a colourless liquid with a camphor-like odour, and D^{15} 1·215. F. M. G. M.

Magnesium Derivative of Fluorene. VICTOR GRIGNARD and CHARLES COURTOT (*Compt. rend.*, 1911, **152**, 1493—1495).—Fluorene forms a magnesium derivative when heated at 135° with magnesium ethyl bromide in xylene. In addition to fluorenecarboxylic acid, the following substances have been obtained from it by the usual methods.

tert.-*Fluorenylfluorenol*, rose-coloured crystals, m. p. 195—196°; the corresponding *ethyl ether*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>C(OEt)\cdot CH<\!\!\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$, crystallises in yellow needles, m. p. 174°; the *chloride* forms pale yellow crystals, m. p. 157—158°. *Fluorenyldiphenylcarbinol* was prepared in the same way as the corresponding indenyl derivative (this vol., i, 193).

tert.-1-*Indenylfluorenol* forms a *methyl ether*, m. p. 115—116°, when its solution in methyl alcohol is treated with hydrogen chloride; under the same conditions diphenyl-1-indenylcarbinol undergoes dehydration. In general, the *tert.*-fluorenols are more stable than the corresponding diphenylcarbinols. W. O. W.

Chlorides and Bromides of Diphenyl Sulphide. KARL FRIES and WILHELM VOGT (*Annalen*, 1911, **381**, 337—346. Compare Böeseken, this vol., i, 41; Fromm and Raiziss, Abstr., 1910, i, 554).—Diphenyl sulphide combines with chlorine when the dry gas is led into a benzene solution of the sulphide; the *dichloride*, SPh_2Cl_2, thus obtained forms pale yellow, flat prisms, which decompose when warmed, yielding mono- and di-chloro-substituted derivatives of diphenyl sulphide. In contact with atmospheric moisture, they yield hydrogen chloride and diphenylsulphoxide.

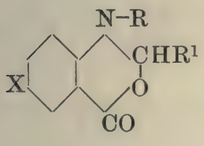
4 : 4′-*Dichlorodiphenylsulphide dichloride*, $SCl_2(C_6H_4Cl)_2$, obtained from either diphenyl sulphide or its 4 : 4′-dichloro-derivative, forms compact, yellow, prismatic crystals, m. p. 95° (decomp.), and on treatment with water yields 4 : 4′-*dichlorodiphenylsulphoxide*, $SO(C_6H_4Cl)_2$, which crystallises from light petroleum in compact prisms, m. p. 143°. The sulphoxide yields a pale violet-coloured solution in concentrated sulphuric acid, and is readily reduced to the sulphide by means of hydrobromic acid.

Diphenyl sulphide dibromide, SPh_2Br_2, obtained by the action of bromine on a well-cooled solution of diphenyl sulphide in hexane, forms orange-coloured needles, and even at the ordinary temperature passes over into substituted derivatives of diphenyl sulphide.

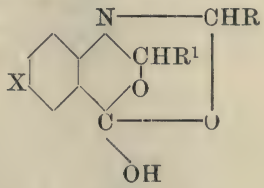
4 : 4′-*Dibromodiphenyl sulphide dibromide*, $C_{12}H_8Br_4S$, forms glistening, dark red plates, and yields a *perbromide*, $C_{12}H_8Br_6S$, in the form of brownish-red prisms.

4 : 4′-*Dibromodiphenylsulphoxide*, $SO(C_6H_4Br)_2$, separates from alcohol in compact, glistening, lance-shaped crystals, m. p. 152°, which dissolve readily in concentrated sulphuric acid, yielding a pale violet solution. J. J. S.

Preparation of Anthranilic Acid Esters Containing a Substituted Group in the para-Position to the Amino-group. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 231687).—When the aldehydo-condensation products of para-substituted anthranilic acids with the constitution I or II (where R and R_1 are hydrogen, alkyl,



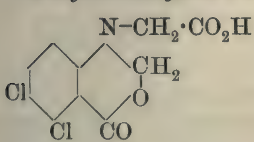
(I.)



(II.)

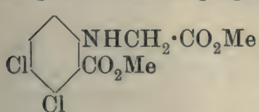
aryl, or alkylaryl groups) are treated with esterifying agents, the aldehydo-groups are eliminated and the corresponding anthranilic ester obtained.

Anhydromethylene - 3 : 4 - dichlorophenylglycine - 2 - carboxylic acid



(annexed formula), m. p. 246° (decomp.), separates in long needles when a warm methyl-alcoholic solution of 3 : 4-dichlorophenylglycine-2-carboxylic acid (264 parts) is treated with 30% formaldehyde solution (105 parts).

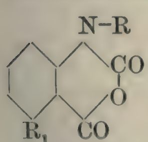
Methyl 3 : 4-dichlorophenylglycine-2-carboxylate (annexed formula), m. p. 76—78°, is prepared by heating the foregoing anhydro-base in



methyl-alcoholic solution with concentrated sulphuric acid at 70° during twelve to fifteen hours, any acid ester which is simultaneously produced being removed subsequently by careful treatment with an alkali hydroxide.

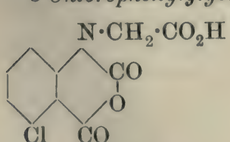
Methyl tetrachloroanthranilate, $NH_2\cdot C_6Cl_4\cdot CO_2Me$, needles, m. p. 120—121°, is obtained by heating tetrachloroanthranilic acid with a mixture of methyl alcohol, methylal, and sulphuric acid at 40—50° during twenty-four hours. F. M. G. M.

Preparation of Substituted Anthranilic Acid Esters. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 231962. Compare Abstr., 1889, i, 996; 1899, i, 939).—It is found that



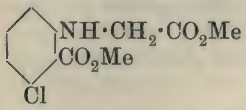
substituted anthranilic acid esters may be obtained in quantitative yield by treating the isatoic acids of the annexed general formula (where R is hydrogen, alkyl, aryl, or alkylaryl groups, and R_1 is a halogen) with esterifying agents.

3-Chlorophenylglycine-2-carboxylic acid, leaflets, m. p. 175° (prepared



from 6-chloroanthranilic acid), when treated with carbonyl chloride in alkaline solution yields 6 - *chloroisatoacetic acid* (annexed formula), a colourless, insoluble powder, which when allowed to remain several days in methyl alcohol with concentrated sulphuric

acid slowly dissolves and is converted into *dimethyl 3-chlorophenylglycine-2-carboxylate* (annexed formula), prisms, m. p. 55—56°.



6-Chloroanthranilic acid on treatment with carbonyl chloride yields 6-*chloroisatoic anhydride*, sparingly soluble leaflets, decomposing at about 280°, which on esterification is converted into *methyl 6-chloroanthranilate*, $NH_2 \cdot C_6H_3Cl \cdot CO_2Me$, a pale yellow oil, b. p. 156—159°/10 mm. F. M. G. M.

Mono- and Di-ethyl Esters of Diphenylitaconic Acid. HANS STOBBE (*Ber.*, 1911, **44**, 1297—1300).—*α-Ethyl β-hydrogen γ-diphenylitaconate*, $CPh_2\colon C(CO_2H) \cdot CH_2 \cdot CO_2Et$, prepared by boiling diphenylitaconic anhydride with alcohol, has m. p. 130—131°; when treated with bromine, it yield *β-bromo-γ-diphenylparaconic acid.* It differs from the correspondirg α-ester (Abstr., 1899, i, 900) in being more sparingly soluble in water, and in crystalline form; the α-ester forms rhomboidal plates, whilst the β-ester crystallises in monoclinic needles.

Improvements in the method of preparation of the α-ester and of ethyl γ-diphenylitaconate are also described. F. B.

Methyl Phenyliminomalonate and its Reactions. RICHARD S. CURTISS and F. GRACE C. SPENCER (*J. Amer. Chem. Soc.*, 1911, **33**, 985—992).—It has been shown in an earlier paper (Abstr., 1909, i, 764) that when methyl anilinotartronate is treated with phosphoric oxide, it is converted into methyl phenyliminomalonate,

$$NPh\colon C(CO_2Me)_2.$$

The compound is thus obtained as a thick, yellow oil; it reacts vigorously with water, alcohols, ammonia, hydrogen chloride, amines, and acids, with formation of colourless, substituted anilinomalonates. The reactivity of this substance is shown to be analogous to that of phenylcarbimide.

When methyl phenyliminomalonate is treated with aniline, methyl dianilinomalonate (Conrad and Reinbach, Abstr., 1902, i, 211) is produced. This compound can also be obtained by the action of aniline on methyl dihydroxymalonate.

Methyl phenyliminomalonate absorbs water from the air, thereby becoming converted into a mixture of methyl dianilinomalonate and methyl dihydroxymalonate.

It has been shown previously (Curtiss, Abstr., 1897, i, 556) that when a solution of ethyl anilinomalonate in light petroleum is heated with freshly precipitated mercuric oxide, the latter undergoes reduction and ethyl dianilinomalonate is produced. It has now been found that when methyl anilinomalonate is treated similarly, the reduction of the mercuric oxide proceeds more slowly and less completely, and a mixture of methyl dihydroxymalonate and dianilinomalonate is produced.

When dry ammonia is passed into an ethereal solution of methyl phenyliminomalonate, a white, crystalline compound and a red, gummy substance are formed. The former is very unstable, and seems readily to undergo polymerisation. Hydrogen chloride reacts with methyl phenyliminomalonate with production of an unstable, crystal-

line compound, which rapidly loses hydrogen chloride on exposure to the air, and changes into gummy polymerisation products. This polymerisation of methyl phenyliminomalonate appears to be analogous to that of phenylcarbimide.

By the action of ethyl alcohol on methyl phenyliminomalonate, a colourless, crystalline *compound*, m. p. 88° (uncorr.), probably $OEt\cdot C(CO_2Et)_2\cdot NHPh$, is produced, which gradually becomes yellow when left in a desiccator. E. G.

Position of the Substituents in α-Resodicarboxylic Acid. PAUL WAITZ (*Monatsh.*, 1911, 32, 427—434).—The identification of Senhofer and Brunner's α-resodicarboxylic acid as 2 : 6-dihydroxybenzene-1 : 3-dicarboxylic acid has been achieved : (1) by heating β- and γ-resorcylic acids separately with ammonium carbonate and water at 130° in closed vessels, whereby α-resodicarboxylic acid is obtained in each case ; (2) by heating α-resodicarboxylic acid with water in sealed tubes, whereby it is decomposed into carbon dioxide and β- and γ-resorcylic acids. C. S.

Derivatives of Nitrohemipinic Acid. RUDOLF WEGSCHEIDER and ALFONS KLEMENC (*Monatsh.*, 1911, 32, 377—401).—Since boiling aniline hydrolyses nitrated phenolic ethers (Abstr., 1910, i, 670), its action on nitrohemipinic acid has been examined. After one hour methylaniline and a substance insoluble in concentrated potassium hydroxide are obtained as by-products, the chief product being 6-*nitromethylnorhemipin*-2-*anilic acid* (6-*nitro*-3-*hydroxy*-4-*methoxyphthal*-2-*anilic acid*), $CO_2H\cdot C_6H(NO_2)(OH)(OMe)\cdot CO\cdot NHPh$, microscopic prisms, m. p. 183—184° (decomp.) ; occasionally the substance merely darkens at 180°, and melts without decomposition at 214°, due probably to the formation of the anil (see below). The anilic acid behaves as a dibasic acid, forms blood-red solutions in alkalis, and does not give a colour reaction with ferric chloride. It yields nitromethylnorhemipinic acid when boiled with water, and forms a disilver *salt*, which is converted by methyl iodide into *methyl* 6-*nitrohemipin*-2-*anilate*, $C_{17}H_{16}O_7N_2$, m. p. 148—149°.

A moist ethereal solution of acetylnitromethylnorhemipinic anhydride (see below) and aniline, after two hours' boiling, yields yellow needles of a mixture, m. p. 197—198°, of the aniline salts of 6-nitromethylnorhemipin-1-anilic acid and its acetyl derivative. The same mixture, which is also produced by working in benzene or without a solvent, yields 6-*nitromethylnorhemipin*-1-*anilic acid* by treatment with potassium hydroxide and subsequent acidification of the red solution. The acid has m. p. 192° (decomp.), resolidifies, and melts again at 213°, the m. p. of the anil below. It differs from the preceding isomeride in behaving as a monobasic acid, and in developing a ruby-red coloration with ferric chloride, a sign that the hydroxyl and carboxyl groups are in the ortho-position to one another. 6-Nitromethylnorhemipin-1-anilic acid forms a sparingly soluble *ammonium* salt, m. p. 229—230° (decomp.), a *silver* salt, and a *disilver* salt ; from the two silver salts methyl iodide produces *methyl* 6-*nitromethylnorhemipin*-1-*anilate*, m. p. 192—193° (decomp.), and *methyl* 6-*nitrohemipin*-1-*anilate*, m. p. 170°

(decomp.), respectively, neither of which gives a colour reaction with ferric chloride.

The following facts prove that 6-nitromethylnorhemipin-1-anilic acid and 6-nitromethylnorhemipin-2-anilic acid are derived from the same nitromethylnorhemipinic acid. (i) Both yield the same 6-*nitromethylnorhemipinanil*, $NO_2\cdot C_6H(OH)(OMe){<}{\scriptsize\begin{matrix}CO\\CO\end{matrix}}{>}NPh$, m. p. 214—215°, when heated in boiling xylene. The anil, which does not give a ferric chloride reaction, is also obtained by heating methyl 6-nitromethylnorhemipin-1-anilate at 198°, or by boiling nitromethylnorhemipinic acid with aniline. (ii) Both react with acetic anhydride and two drops of sulphuric acid on the water-bath to form nitromethylnorhemipinic acid and the acetylated *anil*, $C_{17}H_{12}O_7N_2$, m. p. 212—213°, the latter of which is also produced by acetylating nitromethylnorhemipinanil under the preceding conditions. The hydrolysis of the acetylated anil by aqueous potassium hydroxide (2 mols.) yields 6-nitromethylnorhemipin-2-anilic acid (this is evidently a method whereby 6-nitromethylnorhemipin-1-anilic acid can be converted through the acetylated anil into the isomeric 2-anilic acid, and yields a purer product than the method described above); when hydrolysed by 1 mol. of potassium hydroxide, the acetylated anil yields 6-nitromethylnorhemipinic acid identical with that obtained from nitromethylnoropianic acid by Elbel or by the nitration of methylnorhemipinic acid.

6-Nitromethylnorhemipinic acid is obtained best by passing hydrogen chloride for fifteen hours through a mixture of nitrohemipinic acid and concentrated hydrochloric acid on the water-bath. It has m. p. 205—206° (decomp.) (Elbel gives 220°), and its silver salt and methyl iodide yield *dimethyl 6-nitromethylnorhemipinate*, m. p. 145—146°, which contains a free hydroxyl group, but does not give a coloration with ferric chloride. The acid is not acetylated by acetic anhydride and sodium acetate or 2 drops of sulphuric acid, but is converted by boiling acetyl chloride into *acetylnitromethylnorhemipinic anhydride*, $C_{11}H_7O_8N$, m. p. 165—166°, which is easily hydrolysed to nitromethylnorhemipinic acid by boiling water. C. S.

Methylenedisalicylic Acid [Methanedisalicylic Acid] and its Reaction with Bromine and Iodine. ERIK CLEMMENSEN and ARNOLD H. C. HEITMAN (*J. Amer. Chem. Soc.*, 1911, 33, 733—745).—Methanedisalicylic acid was first prepared by Geigy (D.R.-P. 49970) by heating salicylic acid with a large excess of formaldehyde in presence of concentrated hydrochloric acid, and was afterwards studied by Kahl (Abstr., 1898, i, 259) and Madsen (Abstr., 1907, i, 424). It is now shown that the acid can be obtained in good yield by the interaction of formaldehyde (1 mol.) with salicylic acid (1 mol.) in presence of 50% sulphuric acid. If the reaction is carried out in very concentrated solution, a *compound* is produced which has the same empirical formula as methanedisalicylic acid, and does not melt but chars above 260°. When methanedisalicylic acid is heated either above its m. p. or with potassium hydroxide, it is decomposed into hydroxyphenylmethanesalicylic acid, 4 : 4′-dihydroxydiphenylmethane,

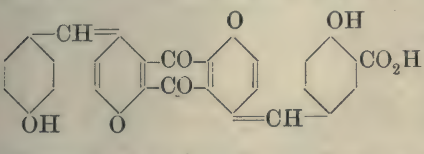
and carbon dioxide. *Calcium, dicalcium, barium, di-barium, magnesium,* and *zinc* methanedisalicylates are described. The *di-acetyl* derivative, m. p. 142°, forms a white, amorphous powder.

Hydroxyphenylmethanesalicylic acid (*hydroxyphenylhomosalicylic acid*), $OH \cdot C_6H_4 \cdot CH_2 \cdot C_6H_3(OH) \cdot CO_2H$, m. p. above 60°, is a pale red, amorphous substance.

The following compounds were obtained by the action of bromine and iodine respectively on methanedisalicylic acid in presence of alkali hydroxide.

Tribromoanthratriquinonedihomosalicylic acid, $C_{30}H_{13}O_{10}Br_3$, is a red, amorphous substance, which decomposes above 200°; its *calcium* salt, $C_{30}H_{11}O_{10}Br_3Ca$, and *potassium* salt, $C_{30}H_9O_{10}Br_3K_4$, are described.

Tri-iodoanthratriquinonedihomosalicylic acid, $C_{30}H_{13}O_{10}I_3$, is a red substance which decomposes above 230°; its *calcium* salt, $C_{30}H_{11}O_{10}I_3Ca$, and *potassium* salt, $C_{30}H_9O_{10}I_3K_4$, were prepared. When this acid is heated in a sealed tube with 1% alkali carbonate or 2% mineral acid, it is converted into a *monocarboxylic acid*, which may be regarded as a tri-iodo-derivative of hydroxybenzylideneanthratriquinonehomosalicylic acid (annexed formula).



Heptabromoanthratriquinonedihomosalicylic acid, $C_{30}H_9O_{10}Br_7$, forms a pale yellow powder and decomposes above 200°; its *potassium* salt, $C_{30}H_5O_{10}Br_7K_4$, is described.

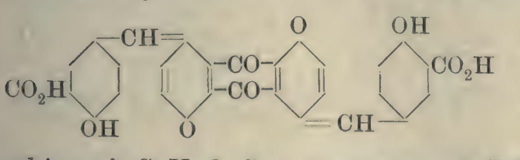
Pentabromohydroxybenzylideneanthratriquinonehomosalicylic acid, $C_{29}H_{11}O_8Br_5$, crystallises in microscopic plates.

Pentaiodohydroxybenzylideneanthratriquinonehomosalicylic acid,

$$C_{29}H_{11}O_8I_5,$$

is a reddish-yellow, amorphous substance; its *potassium* salt, $C_{29}H_{10}O_8I_5K$, forms an olive-green powder.

When tribromoanthratriquinonedihomosalicylic acid is boiled with potassium hydroxide solution and zinc dust, it is converted into *anthratriquinonedihomosalicylic acid* (annexed formula), which forms a brown powder, and decomposes at 185°; the *calcium* salt, $C_{30}H_{14}O_{10}Ca$, and *potassium* salt, $C_{30}H_{12}O_{10}K_4$, are described; the *ethyl* ester forms a colourless, amorphous, resinous mass, and yields a *hexa-acetyl* derivative, m. p. above 70°. E. G.



Derivatives of Amino-acids. IV. Compounds with Glycerol. Emil Abderhalden and Louis Baumann (*Zeitsch. physiol. Chem.*, 1911, 72, 50—57. Compare Abderhalden and Guggenheim, Abstr., 1910, i, 226).—Glycerol monotyrosine forms a crystalline *copper* salt, $C_{24}H_{32}O_{10}N_2Cu$, which gives a red coloration with Millon's reagent even in the cold. *Glycerol* m-*tolyl ether*,

$$OH \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot O \cdot C_6H_4Me,$$

crystallises in long, rectangular plates, m. p. 65—70° (corr.), and

glycerol chloro-m-*tolyl ether*, $C_{10}H_{13}O_3Cl$, crystallises from benzene in groups of needles, m. p. 90° (corr.).

Glyceroldityrosine, $OH\cdot CH[CH_2\cdot O\cdot C_6H_4\cdot CH_2\cdot CH(NH_2)\cdot CO_2H]_2$, obtained by the action of glyceryl-α-dichlorohydrin on the sodium derivative of tyrosine, has not been obtained in a crystalline form. It has m. p. 275° (corr.) (decomp.), and yields a *copper* salt, $C_{21}H_{24}O_7N_2Cu$.

Glycerol di-glycyl-l-*tyrosine*,

$$OH\cdot CH[CH_2\cdot O\cdot C_6H_4\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CO\cdot CH_2\cdot NH_2]_2,$$

prepared by the action of glyceryl-α-dichlorohydrin on the sodium derivative of glycyl-*l*-tyrosine, is precipitated by the addition of alcohol to its aqueous solution, has m. p. 210° and $[\alpha]_D^{20}$ +25·3° in 5% hydrochloric acid. An isomeride, which is sparingly soluble in water, has m. p. 248° and $[\alpha]_D^{20}$ +36·6° in 5% hydrochloric acid.

Glyceryltrityrosine, $C_9H_{10}O_2N\cdot O\cdot CH[CH_2\cdot O\cdot C_9H_{10}O_2N]_2$, crystallises in minute needles, m. p. 295° (corr.). The *hydrochloride* of the *ethyl* ester, $C_{36}H_{47}O_9N_3Cl_3$, is hygroscopic, and has m. p. 83°. J. J. S.

***N*-Phenyl Ethers of the Oximes.** ANGELO ANGELI, LUIGI ALESSANDRI, and M. AIAZZI-MANCINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 546—555).—The formula $R\cdot CH\lt{}^{NR}_{O}$, which is usually ascribed to the *N*-alkylated aldoximes, does not explain the instability of these compounds towards permanganate, to which the oxides, $R\cdot CH\lt{}^{CHR}_{O}$, are stable. It is, further, not in accord with the observation that, in all the more definite and more gentle transformations which these compounds undergo, the oxygen atom is always obtained united with the nitrogen, never with the carbon atom. The authors therefore suggest the formula $R\cdot CH\vdots NR\vdots O$, which is supported by the failure of Scheiber (this vol., i, 382) to prepare these compounds in optically active modifications.

It is found that the action of magnesium phenyl bromide or iodide on the *N*-phenyl or *N*-benzyl derivative of benzaldoxime proceeds according to the scheme: $CHPh\vdots NPh\vdots O \longrightarrow CHPh_2\cdot NPh\cdot OH$, and is hence analogous to the reaction which takes place with benzylideneaniline: $CHPh\vdots NPh \longrightarrow CHPh_2\cdot NHPh$ (compare Busch, Abstr., 1904, i, 663).

β-Phenyl-β-diphenylmethylhydroxylamine, $CHPh_2\cdot NPh\cdot OH$, forms colourless prisms, m. p. 127°, and becomes yellow in the light. When oxidised by means of mercuric oxide, benzaldehyde or magnesium phenyl bromide, it is partly converted into the *compound*, $C_{19}H_{15}ON$, which forms pale yellow leaflets, m. p. 214°, and is also obtained in small proportion in the preparation of the triphenylmethylhydroxylamine. When oxidised with chromic acid, either of these compounds yields nitrosobenzene and benzophenone, whilst, on reduction, diphenylanilinomethane (compare Busch, *loc. cit.*) is obtained. Reduction of the *N*-phenyl derivative of benzaldoxime by means of zinc and ammonium chloride, yields benzylideneaniline; under the same conditions the compound, m. p. 214°, gives a substance, m. p. 83°, having

the same composition as benzophenoneaniline, but differing from it somewhat in its characters.

Oxidation of β-dibenzylhydroxylamine by means of mercuric oxide yields the *N*-benzyl derivative of benzaldoxime, and the action on this of magnesium phenyl bromide gives *β-benzyl-β-diphenylmethylhydroxylamine*, $CHPh_2\cdot N(CH_2Ph)\cdot OH$, forming white crystals, m. p. 105°; on oxidation with mercuric oxide, the latter gives a *compound*, $C_{20}H_{17}ON$, m. p. 159°, which yields benzaldehyde and benzophenone on treatment with chromic acid. T. H. P.

Action of Acid Chlorides and Anhydrides and of Ketones on the Sodium Derivative of Phenylacetonitrile. FERNAND BODROUX (*Compt. rend.*, 1911, **152**, 1594—1596. Compare Abstr., 1910, i, 257, 482, 557, 622, 623).—The sodium derivative of phenylacetonitrile reacts normally with acetyl chloride or acetic anhydride, giving poor yields of α-cyanobenzyl methyl ketone. Benzoyl chloride gives a 95% yield of the corresponding ketone, but phthalic anhydride is without action.

Double decomposition occurs when aliphatic ketones react with the sodium derivative, and the original substances are regenerated on treating the product with water. In the case of the aromatic ketones, however, a molecule of sodium hydroxide is eliminated; thus benzophenone gives $\alpha\beta$-diphenylcinnamonitrile; phenyl *p*-tolyl ketone forms *α-phenyl-β-*p*-tolylcinnamonitrile*, $CN\cdot CPh\colon CPh\cdot C_7H_7$, needles, m. p. 123°; α-naphthyl phenyl ketone gives *α-phenyl-β-α-naphthylcinnamonitrile*, small prisms, m. p. 174—175°. W. O. W.

New Method for Obtaining β-Diketones. ÉMILE ANDRÉ (*Compt. rend.*, 1911, **152**, 1488—1490. Compare this vol., i, 268).—The additive compounds formed by the union of amines with acetylenic ketones behave towards acids in the same way as Moureau and Lazennec's β-aminonitriles (Abstr., 1906, i, 956), giving rise to β-diketones and the salt of an amine. A number of diketones, such as acetylacetophenone and dibenzoylmethane, are readily prepared in this way. W. O. W.

Metallic Compounds of Diaryl Ketones. WILHELM SCHLENK and TOBIAS WEICKEL (*Ber.*, 1911, **44**, 1182—1189).—From the observations of Beckmann and Paul (Abstr., 1892, 169) on the sodium derivatives of diaryl ketones, the authors were led to the conclusion that these compounds contained tervalent carbon, and, in order to support this view, have prepared and examined the chemical behaviour of several new representatives.

p-Phenylbenzophenone (phenyl diphenyl ketone) and di-*p*-phenylbenzophenone (di-diphenyl ketone) combine with sodium in benzene or ethereal solution, yielding strongly coloured *sodium* compounds containing one molecule of ketone combined with one atom of sodium; similar *potassium* compounds have also been prepared. The sodium derivative of di-*p*-phenylbenzophenone, when exposed to air in ethereal solution, at once loses its deep green colour with the formation of sodium peroxide and the original ketone. It readily reacts with

iodine, yielding di-*p*-phenylbenzophenone and sodium iodide. When treated with methyl iodide it is converted into the original ketone and *di-p-phenyldiphenylmethylcarbinol*, $CMe(C_6H_4Ph)_2{\cdot}OH$; with water, it yields the ketone, together with di-*p*-phenylbenzhydrol.

With respect to the constitution of these metallic derivatives of diaryl ketones, the formula $ONa{\cdot}CAr_2{\cdot}CAr_2{\cdot}ONa$ has been proposed by Acree (Abstr., 1903, i, 724). This formula is in agreement with the observation of the authors that the sodium compound of benzophenone, described by Beckmann and Paul (*loc. cit.*) by the direct combination of benzophenone and sodium, is also obtained by the action of sodium amalgam on benzopinacone in ethereal solution, but affords no explanation of the intense colour of these compounds; nor does it explain why the action of water and of methyl iodide, instead of giving rise to pinacones or their methyl ethers in the normal manner, causes a rupture of the molecule between the two central carbon atoms.

A satisfactory explanation of the behaviour of these metallic derivatives is obtained on the assumption that they contain tervalent carbon, and the authors, therefore, propose the constitution

$$-CR_2{\cdot}ONa.$$

This formula accounts for their intense colour and their activity towards oxygen. From analogy with the triarylmethyls, it is assumed that the action of oxygen first leads to the formation of a peroxide, $ONa{\cdot}CAr_2{\cdot}O{\cdot}O{\cdot}CAr_2{\cdot}ONa$, which at once decomposes into sodium peroxide and the ketone $COAr_2$. By the action of water, the metallic derivative gives $-CR_2{\cdot}OH$ as an intermediate product, which either polymerises with the formation of a pinacone, as in the case of the sodium compound of benzophenone, or gives rise to a mixture of ketone and carbinol, $CHR_2{\cdot}OH$, as in the case of the sodium derivative of di-*p*-phenylbenzophenone.

The reaction with methyl iodide is represented as follows:

$$\begin{matrix} ONa{\cdot}CAr_2- \\ ONa{\cdot}CAr_2- \end{matrix} + MeI \longrightarrow \begin{matrix} ONa{\cdot}CAr_2I \\ ONa{\cdot}CAr_2Me \end{matrix} \longrightarrow \begin{matrix} COAr_2 + NaI \\ HO{\cdot}CAr_2Me \end{matrix}.$$

The production of sodium peroxide and anthraquinone by the action of water on the sodium derivative of anthraquinol (Manchot, Abstr., 1901, ii, 93), as well as the formation of anthraquinyl ethyl ether, by the action of ethyl iodide on the same compound (K. Meyer, this vol., i, 193), are explained in a similar manner.

The observation of K. Meyer (*loc. cit*), that the red colour of aqueous solutions of the sodium derivative of anthraquinol increases with rise of temperature, is referred by the authors to a kind of intermolecular dissociation, represented by the scheme:

$$C_6H_4{<}\begin{matrix} C(ONa) \\ | \\ C(ONa) \end{matrix}{>}C_6H_4 \longrightarrow C_6H_4{<}\begin{matrix} | \\ C(ONa) \\ C(ONa) \\ | \end{matrix}{>}C_6H_4,$$

the change here taking place being analogous to that which occurs intramolecularly in the case of triphenylmethyl. F. B.

Anthraquinone Derivatives as Mordant Dyes, and Nature of the Lakes. I. Georg von Georgievics (*Monatsh.*, 1911, 32, 329—345. Compare Abstr., 1905, i, 447).—For eight years the

author has conducted experiments with hydroxyanthraquinones to ascertain the relation between the constitution of a dye and its power of forming lakes with mordants. The following deductions are an amplification of those already recorded.

Firstly, the influence of hydroxyl groups on the colour of the lakes of hydroxyanthraquinones. Hydroxyl groups in the α-positions produce red and blue dyes, in the β-positions yellow and brown dyes; however, an α-hydroxyl group may mask the effect of a β-hydroxyl group, and vice versa. Thus the colour of the lakes of the 1 : 2 : 5-, 1 : 2 : 6-, 1 : 2 : 7-, and 1 : 2 : 8-trihydroxyanthraquinones do not differ materially from those of the lakes of alizarin itself. Anthragallol (1 : 2 : 3-trihydroxyanthraquinone), however, forms brown lakes and so also β-oxyanthragallol, whilst 1 : 2 : 3 : 4-tetrahydroxyanthraquinone, under the influence of the new α-hydroxyl group, again forms red lakes. In fact, the distinction is so sharp between alizarin (and the red-dyeing trihydroxyanthraquinones derived therefrom) and anthragallol and other hydroxyanthraquinones which produce yellow or brown colorations, that a difference in the constitutions of members of the two groups must be conceded. The hydroxyanthraquinones, therefore, are divisible into two groups. One group, comprising anthragallol, β-hydroxyanthragallol, xanthopurpurin, anthrachryson, rufigallol, 1 : 6- and 1 : 7-dihydroxyanthraquinone, and other derivatives forming yellow and brown lakes, has a para-quinonoid structure; for example, anthragallol, $C_6H_4\left<\begin{array}{l}CO\text{——}C{:}C(OH)\cdot CO \\ C(OH){:}C\text{——}CH{:}C\cdot OH\end{array}\right.$ or

$$C_6H_4\left<\begin{array}{l}C(OH){:}C\cdot C(OH){:}C\cdot OH \\ CO\text{——}C{:}CH\text{——}CO\end{array}\right.,$$

whilst the other group, which includes alizarin and its derivatives forming red or blue lakes (except hystazarin, which occupies an intermediate position), has an ortho-quinonoid structure; for example, alizarin, $C_6H_4\left<\begin{array}{l}C(OH){:}C\cdot CO\text{—}C\cdot OH \\ CO\text{——}C{:}CH\cdot CH\end{array}\right.$. In individual hydroxyanthraquinones the tendency to the production of one or other of the quinonoid forms may be such that one and the same dye may be ortho-quinonoid in some of its lakes and para-quinonoid in others; by this means an explanation is found of the fact that, for example, 1 : 6-dihydroxyanthraquinone, which usually yields yellow or brown lakes, produces a strong red tone with a chromium mordant.

With respect to the relation between the positions of the hydroxyl groups and the lake-forming power of the dye, the introduction of another hydroxyl group into a hydroxyanthraquinone may increase or diminish its power of producing lakes. Thus 1 : 2 : 8-trihydroxyanthraquinone forms lakes more readily than alizarin, whilst 1 : 4 : 5 : 8-tetrahydroxyanthraquinone has very little lake-forming power in comparison with 1 : 4 : 5-trihydroxyanthraquinone. Octahydroxyanthraquinone has been prepared (following abstract) and found to exhibit a lake-forming power scarcely more pronounced than that of quinizarin (1 : 4-dihydroxyanthraquinone). This discovery destroys the tenability of Liebermann and Kostanecki's rule; it is true, however, that those members of the hydroxyanthraquinones

which contain hydroxyl groups in the ortho-position are the most pronounced mordant dyes.

Mohlau has disputed the author's statement that hystazarin (2:3-dihydroxyanthraquinone) is a more pronounced mordant dye than 1:3- or 1:4-dihydroxyanthraquinone; in reply, the author shows that quinizarin hardly dyes wool mordanted with tin, whilst hystazarin produces a full orange tone which is fast to milling.

C. S.

Octahydroxyanthraquinone. GEORG VON GEORGIEVICS (*Monatsh.*, 1911, 32, 347—352).—Three parts of rufigallol (1:2:3:5:6:7-hexahydroxyanthraquinone), 100 parts of sulphuric acid (H_2SO_4,H_2O), 4 parts of boric acid, and about 0·05 part of mercuric oxide are heated at 250—260° until a drop of the mixture dissolves in concentrated sulphuric acid with a pure blue colour; the yield of the octahydroxyanthraquinone diminishes rapidly when the heating is too prolonged. The reddish-brown precipitate obtained by pouring the cold mixture into water is washed with boiling water, dried, and crystallised by treating its boiling, saturated solution in pyridine with boiling methyl alcohol and a little water, whereby the dye is obtained in stout, brownish-red needles. *Octahydroxyanthraquinone* can only be crystallised from pyridine or methyl alcohol, yields anthracene by distillation with zinc dust, forms an *octa-acetate*, pale yellow needles, decomp. about 200°, and dissolves in concentrated sulphuric acid, forming a greenish-blue solution (the presence of a red tinge indicates the presence of rufigallol). Its behaviour as a mordant dye has been described (preceding abstract).

C. S.

Preparation of Anthraquinonylglycines. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 232127).—Anthraquinonylglycines may readily be obtained by the action of glyoxylic or thioglyoxylic acid on the corresponding reduced aminoanthraquinones. *β-Anthraquinonylglycine*, orange-yellow crystals, m. p. 236°, is prepared by reducing β-aminoanthraquinone with sodium hyposulphite in aqueous alkaline solution, with the subsequent addition of an alkali glyoxylate and heating during one hour. Unchanged β-aminoanthraquinone is separated by a current of air, and the product precipitated by the addition of mineral acid.

α-Anthraquinonylglycine forms red crystals, m. p. 262° (decomp.).

F. M. G. M.

Desiccation of *cis*-Terpin Hydrate. A. LEULIER (*J. Pharm. Chim.*, 1911, [vii], 3, 440—441).—When terpin hydrate is dried at 100°, part of the terpin formed is volatilised, consequently desiccation should be effected by exposure at atmospheric temperature over sulphuric acid under reduced pressure.

T. A. H.

Sesquiterpene and an Olefinic Camphor Occurring in Southern Cypress. ALLAN F. ODELL (*J. Amer. Chem. Soc.*, 1911, 33, 755—758).—During the course of some work on the oxidation of

cypress (*Taxodium distichum*) sawdust, a fragrant odour was observed, and the present investigation was therefore undertaken.

On extracting cypress sawdust with alcohol, and removing the latter by distillation, a red, viscous product was obtained. By the fractional distillation of this extract under reduced pressure, two new compounds were isolated.

Cypressene, $C_{15}H_{24}$, b. p. 218—220°/35 mm., and 295—300°/778 mm., is a yellowish-green, viscous, nearly odourless liquid, which has D_4^{18} 0·9647, n_D^{22} 1·5240, $[\alpha]_D^{20}$ + 6·53°, reacts violently with moderately strong nitric acid to form a yellow, amorphous oxidation product, and gives a red coloration with concentrated sulphuric acid. The compound contains only one ethylene linking, and is therefore a tricyclic sesquiterpene.

The other new compound, *cypral*, $C_{12}H_{20}O$, is probably an aldehyde. It was obtained as a pale yellow, fragrant, mobile liquid, which has b. p. 182—185°/35 mm., D_4^{20} 0·9469, n_D^{20} 1·5040, is dextrorotatory, and readily reduces ammoniacal solution of silver nitrate. E. G.

Humulene of Oil of Hop Flowers. ERNST DEUSSEN (*J. pr. Chem.*, 1911, [ii], 83, 483—489).—Humulene, b. p. 118—119°/10 mm., isolated from oil of hop flowers by fractional distillation, has been identified with *i*-α-caryophyllene (Abstr., 1908, i, 353; 1909, i, 171, 813) by a comparison of the nitrosates and nitrosochlorides. C. S.

Essential Oil of the Dwarf Pine. ERICH BÖCKER and ALFRED HAHN (*J. pr. Chem.*, 1911, [ii], 83, 489—498).—The oil of the dwarf pine (*Pinus pumilo*), freed from terpenes and sesquiterpenes, and having D^{15} 0·8707, $[\alpha]_D$ − 9°45′, and esterification number 13·4, has been examined with respect to its oxygenated constituents. In addition to *l*-bornyl acetate, it contains aldehydic and ketonic substances, and at least 30% of alcohols and esters of the terpene and sesquiterpene series, as yet unexamined.

The oil has been separated into twelve fractions boiling between 85° and 178°/13 mm. The fractions are dissolved separately in 96% alcohol, and shaken for two to three hours with 30% aqueous sodium hydrogen sulphite. The fraction, b. p. 148—160°/13 mm., $[\alpha]_D$ − 14°15′, esterification number 53, gives by this treatment a small yield of a hydrogen sulphite compound, which after hydrolysis yields an *oil*, $C_{15}H_{26}O$, which is unsaturated and restores the colour of Schiff's reagent. The fractions b. p. 138—148°/13 mm. and 127—138°/13 mm. are united and distilled; the portion b. p. 128—135°/15 mm. yields a hydrogen sulphite compound, from which, by hydrolysis, is obtained a *substance*, $C_{15}H_{24}O$, which is lævorotatory, unsaturated, and probably of ketonic nature.

The fractions b. p. 105—109°, 109—113°, 113—118°, and 118—127°, all under 13 mm., do not yield hydrogen sulphite compounds, but contain *l*-bornyl acetate.

The fractions b. p. 85—100°/13 mm. and 100—105°/13 mm. differ from all the others by having an intense, peculiar odour. By combining them and distilling, a portion b. p. 87—95°/14 mm. is obtained, which yields a white, crystalline hydrogen sulphite com-

pound. The *substance*, $C_8H_{14}O$, obtained by the hydrolysis of this compound by 20% sodium carbonate, has ketonic properties, and is called *pumilone*. It has b. p. 216—217°/754 mm., D^{15} 0·9314, D^{20} 0·9288, n_D 1·46459, and $[\alpha]_D$ $-15°$. It has a very intense, not unpleasant odour. The odour of the natural dwarf pine oil is mainly due to pumilone, although it is present only to the extent of 1—2%. Pumilone, which is unsaturated and contains one double linking, does not yield characteristic derivatives, except the hydrogen sulphite compound and the *semicarbazone*, m. p. 116—117°. C. S.

Theory of the Vulcanisation of Caoutchouc. F. WILLY HINRICHSEN (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 245—250. Compare Abstr., 1910, i, 330).—The influence of time on the proportion of free sulphur in a sample of vulcanised para-rubber has been examined. The total and free sulphur were estimated in the original material, of which samples were kept for six months under different conditions. The experimental data show that the proportion of free sulphur diminishes with time, and that the rate of diminution is much greater at 70° than at room temperature. These observations agree with the author's view, that the sulphur present in the vulcanised caoutchouc is partly adsorbed, the remainder being chemically combined. The adsorption equilibrium is attained very quickly, but the chemical action at low temperatures is relatively a very slow process. As the chemical reaction proceeds, the proportion of free sulphur gradually diminishes. H. M. D.

Cold Vulcanisation. F. WILLY HINRICHSEN (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 250—251).—Polemical against Bysoff (compare this vol., i, 390). H. M. D.

Properties of Dammar Resins. CHARLES COFFIGNIER (*Bull. Soc. chim.*, 1911, [iv], 9, 549—561. Compare Abstr., 1902, i, 633).—The solubilities and analytical constants of some commercial dammar resins are recorded.

Dammar resin from Padang has D^{18} 1·036, m. p. 95°, acid number 31·4, and saponification number 33·7; that from Borneo has D^{18} 1·048, m. p. 120°, acid number 35·1, and saponification number 64·5. Singapore Dammar has D^{18} 1·057, m. p. 95°, acid number 30·1, and saponification number 39·3 Pontianac Dammar has D^{18} 1·025, m. p. 110°, acid number 19·9, and saponification number 30·9. Sumatra Dammar has D^{18} 1·004, m. p. 190°, acid number 59·6, and saponification number 64·5. Batjan Dammar has D^{18} 1·032, m. p. 105°, acid number 18·5, and saponification number 19·6. The solubilities of these dammars in twelve solvents are recorded, and similar data for a number of solvents are given in the cases of Batavian dammar, sandarac, and mastic resins. T. A. H.

Constitution of Bixin. J. F. B. VAN HASSELT (*Rec. trav. chim.*, 1911, 30, 1—47. Compare Marchlewski and Matejko, Abstr., 1906, i, 760).—The author has obtained bixin from anatto by Zwick's process (Abstr., 1900, i, 513) in large, violet, triclinic crystals, m. p.

187°. The analytical data and the molecular weight by the ebullioscopic method in chloroform point to a formula $C_{29}H_{34}O_5$. Etti and Zwick describe mono- and di-potassium derivatives of bixin, and therefore consider that bixin behaves like a dibasic acid. This is not so, the di-potassium compound being a derivative of a new substance, called norbixin, obtained from bixin by the substitution of its methoxyl methyl group by potassium. When bixin is dissolved in boiling aqueous potassium hydroxide, methyl alcohol is evolved, and is detected as formaldehyde after oxidation; by acidifying the alkaline solution, *norbixin*, $C_{28}H_{32}O_5$, is precipitated. It is a light red, crystalline powder, decomp. 240°, and is insoluble in chloroform.

When a solution of bixin (or of purified anatto) and an equivalent amount of potassium hydroxide, dissolved in boiling methyl alcohol, are treated first with ethyl acetate and then with methyl sulphate and a little potassium hydroxide, *bixin methyl ether*, $C_{30}H_{36}O_5$, m. p. 156°, is obtained. It crystallises in red, pleochroic rhomboids, develops an intense blue coloration with concentrated sulphuric acid, and is hydrolysed by alcoholic potassium hydroxide, yielding norbixin. (*bixin ethyl ether*, $C_{31}H_{38}O_5$, m. p. 138°, prepared in a similar manner, forms violet crystals.) By treatment with methyl sulphate, norbixin yields bixin and bixin methyl ether. Bixin contains one methoxy-group, bixin methyl ether two, and norbixin none.

The preceding transformations show that the relation between norbixin, bixin, and bixin methyl ether is expressed by the formulæ OH·R·OH, OH·R·OMe, and OMe·R·OMe, where R is $C_{28}H_{30}O_3$. When a solution of potassium norbixin, obtained by hydrolysing bixin with alcoholic potassium hydroxide, is treated with ethyl sulphate, the precipitate contains *norbixin diethyl ether*,

$$C_{28}H_{30}O_3(OEt)_2,$$

blue rhomboids, m. p. 121°, whilst *norbixin ethyl ether*,

$$C_{28}H_{30}O_3(OEt)\cdot OH,$$

red needles, m. p. 176°, is obtained by acidifying the mother liquor. The latter is quite analogous to bixin in its behaviour, but is more slowly hydrolysed by potassium hydroxide.

The two hydroxyl groups in norbixin are not symmetrically situated in the molecule, since two isomeric norbixin methyl ethyl ethers have been obtained. The one is bixin ethyl ether, m. p. 138°, described above; the other, iso*bixin ethyl ether*, m. p. 149°, is prepared by methylating norbixin ethyl ether, and crystallises in large, red rhomboids. It follows, therefore, that an isomeride of bixin itself should be capable of existence. This isomeride, iso*bixin*, OH·$C_{28}H_{30}O_3$·OMe, m. p. 178°, is obtained by the partial hydrolysis of bixin methyl ether by alcoholic potassium hydroxide; its points of difference from bixin are recorded in the sequel, the most important being its stability to aqueous potassium hydroxide. When *iso*bixin is treated with ethyl sulphate, norbixin diethyl ether, m. p. 121°, is produced, the methyl group having been ousted by an ethyl group.

The potassium derivative, OK·$C_{28}H_{30}O_3$·OH, of bixin is easily obtained by heating a methyl-alcoholic solution of bixin just to the b. p. with an excess of potassium hydroxide; it crystallises in violet needles, and is quite insoluble in boiling water. The dipotassium

derivative of norbixin is formed when bixin is hydrolysed by aqueous or ethyl-alcoholic potassium hydroxide or by treating ethyl-alcoholic norbixin with this alkali; it forms a felted mass of reddish-brown crystals, dissolves easily in water, and oxidises readily in the air. The *disodium* derivative of norbixin and the *potassium* derivatives of norbixin, norbixin ethyl ether, and *iso*bixin are also described.

The unstable orange product, m. p. 200·5°, obtained by Marchlewski and Matejko (*loc. cit.*) by reducing bixin with zinc and acetic acid, is *dihydrobixin*, $C_{29}H_{36}O_5$; it is also formed when the reduction is performed in alkaline solution.

Dihydrobixin methyl ether, $C_{30}H_{38}O_5$, m. p. 174°, *dihydro*iso*bixin*, $C_{29}H_{36}O_5$, m. p. 190°, and *dihydronorbixin*, $C_{28}H_{34}O_5$, decomp. 235°, are obtained by reducing the corresponding bixins with zinc and acetic acid; the last, however, is obtained best by reduction in alkaline solution. All of them are unstable, yellow, crystalline substances, which develop intense blue colorations with concentrated sulphuric acid.

By bromination in cold glacial acetic acid, bixin forms a *decabromide*, $C_{29}H_{34}O_5Br_{10}$, a white, amorphous powder, which does not develop a coloration. Four, six, or eight of the bromine atoms can be eliminated by the more or less prolonged action of zinc and dilute sulphuric acid, the products of reduction being amorphous orange substances, which give a blue coloration with sulphuric acid. Bixin-methyl ether also forms a *decabromide*, $C_{30}H_{36}O_5Br_{10}$, a white powder insoluble in potassium hydroxide. By treatment with iodine chloride in acetic acid, bixin, norbixin, methylbixin, and their dihydro-derivatives, and *iso*bixin all combine with 10 atoms of halogen; consequently hydrogen must attack the molecule of bixin in a different manner from the halogens.

When heated by itself at 190° or in diphenylamine, bixin loses its colour and decomposes into *m*-xylene and a resinous substance, m. p. 145°, which is shown to be a mixture; *iso*bixin, norbixin, the bixin-alkyl ethers, and their dihydro-derivatives also yield *m*-xylene under the same conditions.

The author is unable to confirm Zwick's statements that palmitic acid is produced by the action of steam on bixin at 160° and by the action of light on its sodium derivative. Although the behaviour of bixin with methyl sulphate indicates the presence of a hydroxyl group, attempts to acetylate or benzoylate the substance have been unsuccessful. The failure of bixin methyl ether to react with phenylhydrazine, hydroxylamine, semicarbazide, and magnesium ethyl bromide points to the absence of a carbonyl group. The action of numerous oxidising agents on bixin has been examined; characteristic products, however, have not been isolated. C. S.

The Chlorophyll Group. IV. Phylloporphyrin. LÉON MARCHLEWSKI and J. ROBEL (*Biochem. Zeitsch.*, 1911, 32, 204—221).—The authors describe various modifications of the methods published previously for preparing phylloporphyrin. The most convenient method is from a partly purified phyllotaonin obtained by the method of Kózniewski and Marchlewski. The results of detailed spectro-

scopic examination of phyllo- and meso-porphyrin are given, and also a comparison is made of the results of Willstätter and Fritsche's porphyrins. The paper is controversial as regards the homogeneity of the products obtained by the different investigators. S. B. S.

The Existence of Two Chlorophyllans. LÉON MARCHLEWSKI (*Biochem. Zeitsch.*, 1911, **32**, 332—333).—Controversial. Reply to Tsvett. S. B. S.

The Solubility of the Chlorophyllins and a New Method for Isolating Them. M. TSVETT (*Ber.*, 1911, **44**, 1124—1127).—The chlorophyllins are insoluble in pure light petroleum, but dissolve readily in this solvent in the presence of a small quantity of alcohol, ether, or benzene. Substances having a similar influence on the solubility must be present in the chloroplasts, since the chlorophyllins may be extracted from the freshly-crushed leaves with pure light petroleum.

These substances may be removed by washing the petroleum solutions first with 80% alcohol and finally with water; the mixture of α- and β-chlorophyllins then becomes insoluble, and separates out. In this manner a waxy mixture has been obtained from *Cytisus* leaves, probably identical with a substance mentioned by Willstätter and Stoll (this vol., i, 141), and having similar properties. F. B.

Natural Dyes and Colouring Matters of the Philippines. BENJAMIN T. BROOKS (*Philippine J. Sci.*, 1910, **5**, 439—452).—Annatto, old fustic or morin, indigo, and Brazil wood are four of the principal natural dyes occurring in the Philippines which have not as yet entirely been displaced by the synthetic articles.

An alcoholic extract of narra wood, *Pterocarpus* spp., was found to contain a resin, a tannin, an amorphous, red colouring matter, two colourless, crystalline substances, and a yellow, fluorescent substance.

The red colouring matter, which is named *narrin*, swells and chars at about 180°, yields phloroglucinol and resorcinol by fusion with potassium hydroxide and vanillin by oxidation with alkaline potassium permanganate, produces a small amount of resorcinol dimethyl ether by distillation with zinc dust, and forms a brown, amorphous benzoyl derivative. A comparison of narrin with santalin, isolated from *P. santalinus*, shows that the two substances are closely related. Both are decolorised by zinc and potassium hydroxide or by sodium amalgam in dilute alcohol, yielding solutions in which the colour is restored by atmospheric oxidation; both yield potassium salts by precipitation of their alcoholic solutions by alcoholic potassium acetate. The *copper* salt of santalin has the formula $Cu(C_{15}H_{13}O_5)_2$, whilst that of narrin contains only 6·24% of copper. The dyeing properties of the two substances are very similar. Narrin is insoluble in water, but dissolves in alkaline solutions. Metallic mordants, such as chromium and copper hydroxides, are the most suitable, but the shades are not very fast to soap.

The two colourless, crystalline substances are shown to be pterocarpin and homopterocarpin. Pterocarpin has the formula $C_{14}H_{12}O_4$

and m. p. 163°. Cazeneuve and Hugonenq (Abstr., 1887, 971; 1889, 160) state that it has the composition $C_{20}H_{16}O_6$, and m. p. 152°. Homopterocarpin, $C_{17}H_{16}O_4$, m. p. 86° (Cazeneuve and Hugonenq, *loc. cit.*, give $C_{24}H_{24}O_6$, and m. p. 82—86°), is insoluble in concentrated potassium hydroxide, but yields a little resorcinol at 200—210°. It produces resorcinol dimethyl ether by distillation with zinc dust, but does not react with phenylhydrazine or phosphorus pentachloride. Probably it is closely related to narrin. C. S.

Reduction of Biliary Pigments by the Hydrogen Evolved from Palladium, Hydrogenised in Presence of Sodium Hypophosphite: Formation of Urobilinogen. JULES VILLE (*Bull. Soc. chim.*, 1911, [iv], 9, 480—483).—To a solution of pigments obtained from biliary calculi from a cow, sodium hydroxide and palladium, precipitated from the chloride by means of sodium hypophosphite, were added, and the whole warmed to 100°. Into this sodium hypophosphite solution was gradually introduced. In a short time urobilinogen was formed, and could be detected by Erhlich's reagent, or by its conversion into urobilin and observation of the characteristic absorption spectrum of the latter. The reaction also takes place in the cold, but more slowly. T. A. H.

Catalytic Isomerisation of Acetylenic Pinacone [$\beta\epsilon$-Dimethyl-Δ^{γ}-hexinene-$\beta\epsilon$-diol]. Synthesis of 3-Keto-2:2:5:5-tetramethyltetrahydrofuran. GEORGES DUPONT (*Compt. rend.*, 1911, 152, 1486—1488. Compare this vol., i, 173).—When dimethyl-Δ^{γ}-hexinene-$\beta\epsilon$-diol is heated with an aqueous solution of mercuric sulphate and the mixture distilled in steam, a mobile liquid is obtained, having a camphoraceous odour, m. p. −20·5°, b. p. 149°, D^{18} 0·9251, n_D^{18} 1·4198. This is not the expected dihydroxy-ketone, but an internal anhydride, 3-*keto*-2:2:5:5-*tetramethyltetrahydrofuran*,

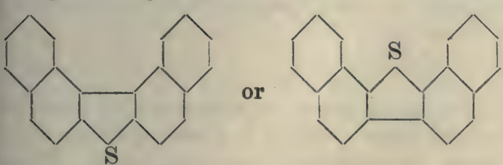
$$\begin{array}{l}CO{-}CMe_2 \\ | \\ CH_2{\cdot}CMe_2\end{array}\!\!>\!O,$$

a very stable substance, yielding a *semicarbazone*, needles, m. p. 190°, an *oxime*, leaflets, m. p. 128°, and a *phenylhydrazone*, m. p. 134°. When treated with magnesium methyl bromide it forms a tertiary alcohol, m. p. 77°, identical with that obtained from $\beta\gamma\epsilon$-trimethylhexane-$\beta\gamma\epsilon$-triol (Bouveault and Locquin, this vol., i, 2). The ketone is converted by the magnesium derivative of acetylene dibromide into a *substance*, $C_8H_{15}O_2{\cdot}C{⋮}C{\cdot}C_8H_{15}O_2$, m. p. 97—98°. It also behaves as an enol, giving a normal *sulphate*, $(C_8H_{13}O)_2SO_4$, m. p. 67—70°, a *sodium*, and a *potassium* salt. When the latter is treated with ethyl iodide, 3-*ethoxy*-2:2:5:5-*tetramethyl*-2:5-*dihydrofuran*, $C_8H_{13}O{\cdot}OEt$, is formed as a liquid, b. p. 157—159°, D^{18} 0·8878, n_D 1·4237. W. O W.

Constitution of Thiophenoquinones and Mechanism of Quinone Reactions. THEODOR POSNER (*J. pr. Chem.*, 1911, [ii], 83, 471—483).—Final reply to Michael (Abstr., 1910, i, 748) and to Michael and Cobb (*ibid.*, i, 748). C. S.

Phenothioxin. ENOS FERRARIO (*Bull. Soc. chim.*, 1911, [iv], **9** 536—537).—There is very little interaction when sulphur and diphenyl ether are heated together, unless a catalyst, such as aluminium or magnesium chloride, is present, in which case phenothioxin (Mauthner, Abstr., 1906, i, 447) is formed. Phenothioxin combines with two atoms of hydrogen when reduced, and when heated with copper at 250° forms diphenylene oxide. T. A. H.

Dinaphthathiophen. M. LANFRY (*Compt. rend.*, 1911, **152**, 1254—1256. Compare this vol., i, 151).—From the products of the action of sulphur on naphthalene at a red heat a substance, *dinaphthathiophen*, has been isolated in the form of pearly, yellow scales,



m. p. 250·5° (corr.), b. p. above 440°, without appreciable decomposition. Its constitution is represented by the annexed formula. When the substance is oxidised with chromic acid, it yields phthalic acid. The *hexabromo*-derivative, $C_{20}H_6Br_6S$, m. p. 260°, furnishes 3 : 6-dibromophthalic acid on oxidation.

Boiling nitric acid converts dinaphthathiophen into a yellow *tetranitro*-derivative, $C_{20}H_8(NO_2)_4S$, m. p. about 210°. W. O. W.

Thianthren. KARL FRIES and WILHELM VOGT (*Annalen*, 1911, **381**, 312—337).—Of the five possible oxidation products of thianthren, namely : (i) $C_6H_4{<}^{SO}_{S}{>}C_6H_4$; (ii) $C_6H_4{<}^{SO}_{SO}{>}C_6H_4$;

(iii) $C_6H_4{<}^{SO_2}_{S}{>}C_6H_4$;

(iv) $C_6H_4{<}^{SO_2}_{SO}{>}C_6H_4$; (v) $C_6H_4{<}^{SO_2}_{SO_2}{>}C_6H_4$, the disulphoxide (ii) has been recently shown (this vol., i, 395) to exist in two isomeric forms. Thianthrenmonosulphoxide (i) can be obtained by oxidising a glacial acetic acid solution of thianthren with dilute nitric acid (D 1·2) (compare Fries and Volk, Abstr., 1909, i, 406). The monosulphone (iii) is formed by the action of chlorine on a boiling dilute acetic acid solution of thianthren, and when oxidised with concentrated nitric acid yields the trioxide (iv), which is also formed by the action of chlorine and water on the monosulphoxide or the isomeric disulphoxides.

Thianthren is most readily prepared by a modification of Genvresse's method (Abstr., 1897, i, 240), and yields a *compound*, $C_{12}H_8S_2,FeCl_3$, in the form of glistening, bronzy needles, readily decomposed by water.

Thianthrenmonosulphoxide, $C_{12}H_8OS_2$, crystallises from methyl alcohol or benzene in long needles, m. p. 143°. Its solution in concentrated sulphuric acid has a brownish-red colour, which changes to a deep blue on the addition of a little water. The addition of much water precipitates the original sulphoxide, but when the solutions are kept for some time or warmed, thianthren is formed. When the

solution in concentrated hydrochloric acid is kept for some time, chlorothianthren is deposited, but hydrogen bromide reacts with a glacial acetic acid solution of the sulphoxide, yielding thianthren. *Thianthrenmonosulphone*, $C_{12}H_8O_2S_2$, is best prepared by leading chlorine into a glacial acetic acid solution of thianthren and boiling, each operation being repeated several times. It crystallises from acetic acid in colourless, glistening plates, m. p. 159°, and is quite stable towards hydrogen bromide or zinc dust and acetic acid. Its solution in concentrated sulphuric acid has a rose colour, and does not decompose when kept.

Thianthrensulphonesulphoxide (*thianthrentrioxide*), $C_{12}H_8O_3S_2$, crystallises from alcohol in small, compact prisms, m. p. 216°; its solution in concentrated sulphuric acid is colourless, and with hydrobromic acid it yields the monosulphone.

Thianthren dichloride, $C_6H_4<\genfrac{}{}{0pt}{}{SCl_2}{-S-}>C_6H_4$ or $C_6H_4\lessgtr\genfrac{}{}{0pt}{}{SCl}{SCl}>C_6H_4$, obtained by the action of dry chlorine on a benzene solution of thianthren, forms brilliant red prisms, which are readily affected by moisture, yielding hydrogen chloride and the sulphoxide. When heated alone the crystals decompose into chlorine and thianthren. 4-*Chlorothianthren*, $C_{12}H_7ClS_2$, crystallises from glacial acetic acid in prisms, m. p. 84°, and gives a pale violet-red coloration with concentrated sulphuric acid, but this gradually changes to a deep violet-blue. It can be prepared by the action of chlorine on a chloroform solution of thianthren and exposing the product to the action of atmospheric moisture, or from thianthren sulphoxide and an acetic acid solution of hydrogen chloride. 4 : 4′-*Dichlorothianthren*, $C_{12}H_6Cl_2S_2$, obtained by the action of chlorine on thianthren or its monochloro-derivative, or by the condensation of chlorobenzene and chloride of sulphur in the presence of carbon disulphide and aluminium chloride, crystallises from benzene or glacial acetic acid in long, slender needles, m. p. 171°. It dissolves slowly in concentrated sulphuric acid, and the solution has a brilliant blue colour.

2′-*Ethoxydiphenylsulphone*-2-*sulphinic acid*,

$$SO_2H\cdot C_6H_4\cdot SO_2\cdot C_6H_4\cdot OEt,$$

obtained by boiling thianthrendisulphone (Graebe, *Annalen*, 1875, **179**, 178) with alcohol and 50% potassium hydroxide solution, forms slender needles, m. p. 151° (decomp.), and yields a sparingly soluble *sodium* salt. When reduced with zinc dust and alcoholic hydrochloric acid, the sulphinic acid yields 2′-*ethoxy*-2-*thioldiphenylsulphone*,

$$SH\cdot C_6H_4\cdot SO_2\cdot C_6H_4\cdot OEt,$$

which crystallises from alcohol in small needles, m. p. 131°. Its solutions in alkalis are oxidised rapidly on exposure to the air. The *methyl ether*, $C_{15}H_{16}O_3S_2$, crystallises from benzene in compact needles, m. p. 178°. 2′-*Ethoxydiphenylsulphone disulphide*,

$$(OEt\cdot C_6H_4\cdot SO_2\cdot C_6H_4)_2S_2,$$

obtained by oxidising the thiol with bromine water, crystallises from glacial acetic acid in compact prisms, m. p. 270° (decomp.). 2′-*Ethoxydiphenylsulphone*-2-*sulphonyl chloride*,

$$OEt\cdot C_6H_4\cdot SO_2\cdot C_6H_4\cdot SO_2Cl,$$

prepared by the action of chlorine on a glacial acetic acid solution of the sulphinic acid, crystallises from benzene in brilliant, compact rhombs, m. p. 159°. The corresponding *bromide*, $C_{14}H_{13}O_5BrS_2$, has m. p. 177°, and with excess of bromine yields a substituted *bromide*,

$$C_{14}H_{12}O_5Br_2S_2,$$

which crystallises in needles, m. p. 179°, and yields a *perbromide*, $C_{14}H_{12}O_5S_2Br_4$, in the form of orange-coloured needles. 2′-*Ethoxydiphenylsulphone*-2-*sulphonic acid*, $OEt{\cdot}C_6H_4{\cdot}SO_2{\cdot}C_6H_4{\cdot}SO_3H$, crystallises from glacial acetic acid in compact needles, m. p. 178°. The corresponding *anilide*, $C_{20}H_{19}O_5NS_2$, crystallises in prisms, m. p. 204°.

2′-*Methoxydiphenylsulphone*-2-*sulphinic acid*,

$$OMe{\cdot}C_6H_4{\cdot}SO_2{\cdot}C_6H_4{\cdot}SO_2H,$$

obtained by hydrolysing the disulphone with methyl-alcoholic potash, has m. p. 161° (decomp.). 2′-*Methoxy*-2-*thioldiphenylsulphone*,

$$C_{13}H_{12}O_3S_2,$$

has m. p. 157°, and its *methyl ether*, $C_{14}H_{14}O_3S_2$, m. p. 197°. 2′-*Methoxydiphenylsulphone*-2-*sulphonyl chloride*, $C_{13}H_{11}O_5ClS_2$, forms compact prisms, m. p. 210°, and 2′-*methoxydiphenylsulphone*-2-*sulphonic acid*, $C_{13}H_{12}O_6S_2$, compact needles, m. p. 202°. The *anilide* forms rhombic crystals, m. p. 193°. J. J. S.

Introduction of Several Phthalic Acid Groups into Aromatic Compounds. III. Experiments with Thianthren, Dimethylthianthren, Thiodiphenylamine, and *N*-Methylthiodiphenylamine.

ROLAND SCHOLL and CHRISTIAN SEER (*Ber.*, 1911, 44, 1233—1249. Compare this vol., i, 452, 453).—By the action of phthalic anhydride and aluminium chloride on thianthren in the presence of carbon disulphide, thianthren-2-phthaloylic acid and the 2:6-diphthaloylic acid are formed.

The yield of the dibasic acid is increased by using more anhydride and less carbon disulphide, and heating for twenty-four hours. The mixture of the two acids can be separated by means of their ammonium salts, as the salt of the monobasic acid is sparingly, and that derived from the dibasic acid readily, soluble in water.

Thianthren-2-phthaloylic acid, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_3{<}^{S}_{S}{>}C_6H_4$, crystallises from boiling xylene, has m. p. 219—221°, and dissolves in concentrated sulphuric acid, yielding a violet-coloured solution. When heated with anhydrous zinc chloride for one hour at 230—235°, it yields 2:3-*phthaloylthianthren*, $C_6H_4{<}^{CO}_{CO}{>}C_6H_2{<}^{S}_{S}{>}C_6H_4$, which crystallises from nitrobenzene in brilliant dark red needles, m. p. 253°. With alkaline hyposulphite it gives a dark reddish-brown solution, which does not dye unmordanted cotton.

Thianthren-2 : 6-*diphthaloylic acid*,

$$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_3{<}^{S}_{S}{>}C_6H_3{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H,$$

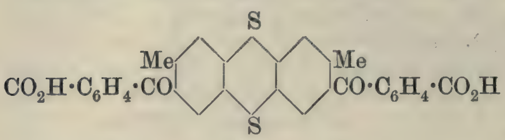
does not crystallise well, has m. p. 143—160°, and gives a dark brown coloration with concentrated sulphuric acid. When heated with

the concentrated acid for forty minutes at 120—124°, it yields 2 : 3 : 6 : 7-*diphthaloylthianthren*,

$$C_6H_4<{CO \atop CO}>C_6H_2<{S \atop S}>C_6H_2<{CO \atop CO}>C_6H_4,$$

This separates from nitrobenzene in minute, brownish-red crystals, which are not molten at 325°. Its solution in concentrated sulphuric acid is grass-green, and its reduction product is dark red, but does not dye unmordanted cotton.

2 : 6-*Dimethylthianthren*-3 : 7-*diphthaloylic acid* (annexed formula),



prepared by heating 2 : 6 - dimethylthianthren (Jacobson and Ney, Abstr., 1894, i, 125), phthalic anhydride, and aluminium chloride, first at 60—100°, and then for seven hours at 100—104°, forms a light red powder, and with concentrated sulphuric acid at 120—124° yields 2 : 6-*dimethyl*-3 : 4 : 7 : 8-*diphthaloylthianthren*, $C_{30}H_{16}O_4S_2$, which crystallises from nitrobenzene in reddish-brown needles, m. p. 380—385° (decomp.). The vat dye obtained by the action of alkaline hyposulphite colours unmordanted cotton yellow.

Phenylsulphidephthaloylic [*phenylthiolbenzoylbenzoic*] *acid*,

$$SPh\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CO_2H,$$

crystallises from light petroleum, and has m. p. 121—122°. The *ammonium* salt is sparingly soluble, and crystallises in glistening needles, m. p. 171°. When warmed at 60° with concentrated sulphuric acid it is largely sulphonated, but with zinc chloride yields *phthaloylphenyl sulphide*, $C_6H_4\colon C_2O_2\colon C_6H_3\cdot SPh$.

Thiodiphenylamine reacts with phthalic anhydride and aluminium chloride in the presence of carbon disulphide, yielding a tribasic acid; two $\cdot CO\cdot C_6H_4\cdot CO_2H$ groups are introduced into the para-positions with respect to the imino-group and meta with respect to the sulphur atom, and the third group becomes attached to nitrogen. When *N*-methylthiodiphenylamine is used, only two phthalic acid groups are introduced.

Thiodiphenylamine-2 : 7-*diphthaloylic acid*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_3<{NH \atop S}>C_6H_3\cdot CO\cdot C_6H_4\cdot CO_2H,$$

prepared by hydrolysing the tribasic acid with 2*N*-sodium hydroxide solution, crystallises from nitrobenzene in brick-red, glistening plates, and turns dark-coloured and decomposes at 250°. 2 : 3 : 6 : 7-*Diphthaloylthiodiphenylamine thiodianthraquinonylamine*,

$$C_6H_4<{CO \atop CO}>C_6H_2<{NH \atop S}>C_6H_2<{CO \atop CO}>C_4H_4,$$

obtained by heating the dibasic acid with concentrated sulphuric acid at 100—106°, crystallises from nitrobenzene, aniline or quinoline, and has m. p. 380°. It is bluish-black when dry, greenish-blue when moist, and yields a dark red vat-dye. Its *sulphonic acid* dyes wool a grey-green.

[With WALTER TRITSCH.]—N-*Methylthiodiphenylamine*-2 : 7-*diphthaloylic acid*, $C_{29}H_{19}O_6NS$, crystallises from cumene, decomposes at

170°, and its solution in concentrated sulphuric acid has an olive-green or in thin layers a reddish-brown colour. With concentrated sulphuric acid at 100—105°, it yields 6 : 7-*phthaloyl-N-methylthiodiphenylamine-2-phthaloylic acid*,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2<\begin{matrix}NMe\\S\end{matrix}>C_6H_2\cdot CO\cdot C_6H_4\cdot CO_2H,$$

which crystallises from nitrobenzene as a violet-black powder. 2 : 3 : 6 : 7-*Diphthaloyl-N-methylthiodiphenylamine*, $C_{29}H_{15}O_4NS$, crystallises from aniline in black needles, m. p. 370°, and gives a dark red vat dye.

Thio-β-dinaphthylamine also condenses with phthalic anhydride and aluminium chloride in the absence of a diluent, yielding a mixture of phthaloylic acids and *thiodinaphthanthraquinoylamine*, from which the amine can be obtained by treatment with concentrated sulphuric acid. It is best purified by reduction and subsequent oxidation, and has a black colour.

mp-*Ditolylamine*, $C_{14}H_{15}N$, obtained by heating *m*-iodotoluene and *p*-toluidine with soda-lime at 335—340° for five hours, and finally for an hour at 370°, yields a *hydrochloride*, $C_{14}H_{16}NCl$, in the absence of water, and has m. p. 202—203°. The base forms a thick oil with b. p. above 300°.

mmp-*Tritolylamine*, $C_{21}H_{21}N$, obtained by heating a mixture of *m*-iodotoluene, *p*-toluidine, and soda-lime for fifteen hours at 320—330°, crystallises from alcohol in colourless needles, m. p. 89—90°, and does not combine with hydrogen chloride.

J. J. S.

Preparation of Acid Esters of Quinine Halogen Additive Products. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 231961).—*Ethyl hydrochloroquininecarboxylate*, $C_{20}H_{24}O_2N_2Cl\cdot CO_2Et$, colourless, tasteless needles, m. p. 124°, soluble in dilute acids and re-precipitated by alkalis, is prepared by boiling a benzene solution of hydrochloroquinine with ethyl chloroformate, dissolving out the product with dilute hydrochloric acid, and re-precipitating with ammonia.

*Ethyl hydrochloro*iso*quininecarboxylate* is prepared similarly, but in the presence of pyridine; it forms large, colourless, tasteless prisms, m. p. 191—192°; its solution in dilute sulphuric acid exhibits a green fluorescence.

Ethyl hydrobromoquininecarboxylate, columnar-shaped crystals, has m. p. 168—169°.

Salicylhydrobromoquinine, $C_{20}H_{24}O_2N_2Br\cdot CO\cdot C_6H_4\cdot OH$, colourless, tasteless powder, m. p. 106—107°, is obtained by allowing quinine ethyl salicylate (1 part) dissolved in five parts of hydrobromic acid (D 1·78) to remain during a week at a temperature of 0° and then extracting the product with ether.

Benzoylhydrobromoquinine salicylate,

$$C_{20}H_{24}O_2N_2Br\cdot COPh,C_6H_4(OH)\cdot CO_2H,$$

red leaflets, m. p. 110—115°, is prepared by leaving a solution of benzoyl quinine (1 part) in three parts of hydrobromic acid (D 1·78) during a fortnight at 0°, extracting with ether, and washing with ammonium

hydroxide; the ethereal solution of *benzoyl hydrobromoquinine* so obtained, is dried and treated with salicylic acid in the same solvent, when the product slowly separates.

Ethyl hydriodoquininecarboxylate, $C_{20}H_{24}O_2N_2I\cdot CO_2Et$, a pale yellow powder, m. p. 74—78°, is obtained by boiling together molecular proportions of hydriodoquinine and ethyl chloroformate in ethereal solution. F. M. G. M.

Intramolecular Change of Quinidine (Conchinine) by Sulphuric Acid. MICHAEL PFANNL (*Monatsh.*, 1911, 32, 241—255).—The intramolecular changes of quinidine and of cinchonidine caused by various means have received far less attention than those of cinchonine. The present paper deals with a change of quinidine. This cannot be accomplished by the usual process of adding on a halogen acid and then eliminating it again by suitable means, because quinidine only dissolves in hydriodic acid at a temperature at which partial demethylation occurs. Pure quinidine sulphate,

$$2C_{20}H_{24}O_2N_2,H_2SO_4,2H_2O,$$

$[\alpha]_j$ 177·5°, therefore, is dissolved in 66·5% sulphuric acid. After two hours at 100°, the specific rotation becomes constant at 22°. The solution is neutralised by ammonia, the liberated bases are extracted with ether, the ethereal solution is washed with water to remove the sulphonated bases (about 17% of which is formed), the ether is distilled off, and an alcoholic solution of the residue is treated with water and neutralised by hydriodic acid. By fractional crystallisation the very sparingly soluble quinidine hydriodide is easily separated from the hydriodide of the new isomeric base, which is called *iso*quinidine. A careful examination of the mother liquor shows that *iso*quinidine is the only isomeride produced.

*iso*Quinidine, $C_{20}H_{24}O_2N_2$, m. p. 142° (corr.), $[\alpha]_j$ $-9°$, crystallises with difficulty, forming long, white needles. It forms a *sulphate*, $2C_{20}H_{24}O_2N_2,H_2SO_4,7H_2O$, $[\alpha]_j$ $-35·5°$, *hydrogen sulphate*,

$$C_{20}H_{24}O_2N_2,H_2SO_4,2H_2O,$$

$[\alpha]_j$ 10·2°, *hydrogen tartrate*, $C_{20}H_{24}O_2N_2,C_4H_6O_6,2H_2O$, and *hydriodide*, $C_{20}H_{24}O_2N_2,HI$, which is five times as soluble as quinidine hydriodide in water at 30°.

In the experiments, 16·5% of the quinidine is lost by sulphonation, 66% is recovered as quinidine and *iso*quinidine, and a further 13·4% in the form of the hydrogen tartrates, leaving only 4% unaccounted for. C. S.

Intramolecular Change of Quinidine (Conchinine) and of Cinchonidine by Sulphuric Acid. FRITZ PANETH (*Monatsh.*, 1911, 32, 257—274. Compare preceding abstract).—The results obtained by Pfannl with quinidine are unchanged when the action of the sulphuric acid is prolonged to nine hours. With 96% sulphuric acid, however, the striking observation is made that quinidine, in the form of its hydrogen sulphate, is not converted into the isomeric *iso*quinidine, but is almost entirely sulphonated. Thus, after forty-six hours at the ordinary temperature, 15% of the quinidine is recovered unchanged,

whilst 80% has been sulphonated. At 75° the results are almost the same; 86% of the base is sulphonated, and 10% is recovered unchanged.

At the ordinary temperature, 66·5% sulphuric acid has scarcely any action on cinchonidine (in the form of the tetrasulphate), but after two hours at 100° it converts the base entirely into sulphonated products (up to 11·5%) and a new isomeride, iso*cinchonidine*, m. p. 252°. (From the agreement of their other properties this base and Hesse's *iso*-cinchonidine, m. p. 235°, may be identical substances.) *iso*Cinchonidine has $[\alpha]_D$ −128° in a mixture of two volumes of chloroform and one volume of 97% alcohol, and forms a *hydriodide*, $C_{19}H_{22}ON_2HI$, m. p. 225° (decomp.), $[\alpha]_D$ − 58° in chloroform–alcohol. Its *sulphate* in neutral solution differs from that of cinchonidine by not yielding a precipitate with potassium sodium tartrate. C. S.

Preparation of Cotarnine Salts of Organic Acids. MARTIN FREUND (D.R.-P. 232003).—Crystalline, well characterised derivatives of cotarnine with hydrogen sulphide, hydrogen peroxide, and hydrogen cyanide have been described (Abstr., 1900, i, 248), but the salts with organic acid have not previously been prepared.

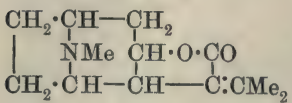
Cotarnine cholate, a yellow powder, m. p. 116—120° (decomp.), is obtained by digesting cotarnine (1 mol.) with cholic acid (2 mols.) in aqueous solution, filtering, and evaporating the solution to dryness in a vacuum.

Cotarnine phthalate, m. p. 102°, is prepared in a similar manner with one molecular proportion of phthalic acid. F. M. G. M.

Constitution of Dioscorine. K. GORTER (*Rec. trav. chim.*, 1911, 30, 161—176. Compare this vol., i, 222).—Its behaviour with hydriodic acid, acetic anhydride, and potassium hydroxide proves that dioscorine does not contain methoxy- or hydroxyl groups, and that it is a γ-lactone. When examined by Hofmann's process of exhaustive methylation, it yields a series of products which indicate that it is a derivative of *cyclo*heptane, not of *cyclo*hexane as suggested previously. Thus by treatment with silver oxide, dioscorine methiodide yields a strongly alkaline hydroxide, which is converted by distillation in a vacuum into carbon dioxide, water, and a new base, *demethyldioscoridine*, $C_{13}H_{21}N$, b. p. 116—120°/8 mm., D_4^{26} 0·8987, n_D^{26} 1·50525. The exaltation of the molecular refraction over that calculated for the formula $C_{13}H_{21}N|\overline{=}_3$ indicates that demethyldioscoridine contains a conjugated double linking. With methyl iodide, demethyldioscoridine yields a methiodide convertible by silver oxide into a hydroxide which is decomposed into trimethylamine and a *hydrocarbon*, $C_{11}H_{14}$, by distillation in a vacuum. Were dioscorine a derivative of *cyclo*hexane this hydrocarbon would certainly be an unsaturated aromatic hydrocarbon; however, it does not yield an aromatic acid by oxidation with potassium permanganate. When a solution of the hydrocarbon in cold acetic acid is saturated with hydrogen bromide, and the yellow liquid additive compound formed is distilled with quinoline in a vacuum, a hydrocarbon is obtained which yields *o*-toluic acid by oxidation with potassium permanganate. This hydrocarbon, then,

should have the constitution $\begin{array}{l}CH{:}CH{\cdot}CMe\\ |\qquad\qquad\ \ \|\\ CH{:}CH{\cdot}C{\cdot}CH{:}C_3H_6\end{array}$, and the original hydrocarbon would be a butenyl*cyclo*heptatriene.

Assuming this to be correct, the author advances reasons for ascribing to dioscorine the annexed constitution. This formula harmonises well with the behaviour of dioscorine and its derivatives recorded above. The presence of the group $\cdot CO\cdot C{:}C<$ suggests that dioscorine should be reduced by sodium amalgam. This is so, an aqueous solution of its hydrobromide yielding *bisdihydrodioscorine*, a saturated *substance*, $(C_{13}H_{20}O_2N)_2$, m. p. 266—267°, the *aurichloride* of which has m. p. 243° (decomp.).



The physiological action of dioscorine is similar to that of picrotoxin, and is connected with the presence of the group $\cdot CO\cdot C{:}C<$. When the double linking is suppressed or when the lactone ring is ruptured, the resulting substances (bisdihydrodioscorine and dioscoric acid respectively) no longer have the property of causing cramp. C. S.

Ephedrine and ψ-Ephedrine. Ernst Schmidt (*Arch. Pharm.*, 1911, **249**, 305—310. Compare Abstr., 1909, i, 322; Rabe, this vol., i, 396).—Dimethylephedrineammonium hydroxide, when heated in a current of steam, furnishes as nitrogen-free product an oil with an odour recalling those of dill and estragon. On treatment with trimethylamine in alcohol at 100°, this oil is, in part, converted into a substance which furnishes an *aurichloride*, $C_9H_{10}ONMe_3,HAuCl_4$, m. p. 190—191°, which crystallises in glancing leaflets, and is sparingly soluble in water. *Dimethylephedrine aurichloride*, m. p. 185—186°, crystallises in yellow needles, and is very soluble in water. The *platinichlorides* prepared from both these substances had m. p. 249—251°, crystallised in long needles, and were sparingly soluble in water. This reaction indicates the presence in the original oil of an alkylene oxide of the formula $O<\begin{array}{l}CHPh\\ |\\ CHMe\end{array}$. The residue of the oil unattacked by trimethylamine contained propiophenone and a third *substance*, possibly the glycol, $C_9H_{10}(OH)_2$, which furnishes a *dibenzoate*, m. p. 83—85°, crystallising in colourless needles (compare Schmidt and Gaze, *Apoth. Zeit.*, 1911, p. 368). T. A. H.

Sparteine. XXIII. Decomposition of *iso*Sparteine α′-Methylhydroxide. XXIV. Methyl*iso*sparteine. Charles Moureu and Amand Valeur (*Bull. Soc. chim.*, 1911, [iv], 9, 476—478, 478—479).—These two papers give experimental details of work already published (this vol., i, 319), and add some new data.

Measurements of the optical rotation of solutions of *iso*sparteine α′-methyl hydroxide, to which 2 mols. of hydrogen iodide have been added, show that it does not undergo isomerisation to the α-methyl hydroxide, in its formation from the α′-methiodide by the action of silver hydroxide.

Methyl*iso*sparteine, the formation of which has been described

already (*loc. cit.*), has m. p. 24°, b. p. 169—170°/13 mm., D_4^{19} 0·9651, n_D 1·5131, $[\alpha]_D$ +23·58° in alcohol. Methyl*i* *o*sparteine dimethiodide (*loc. cit.*), m. p. 281—282°, $[\alpha]_D$ +21·35°, is readily soluble in water or boiling methyl alcohol. T. A. H.

The Relative Stability of the Pyrrolidine Ring. JULIUS VON BRAUN (*Ber.*, 1911, **44**, 1252—1260. Compare Abstr., 1909, i, 507, 604).—The reaction of cyanogen bromide with 1-ethylpiperidine and 1-ethylpyrrolidine proves that the pyrrolidine is less stable than the piperidine ring; for example, 34% of the ethylpiperidine compound is decomposed in such a manner that the ring is ruptured, and from 66% the ethyl group is simply removed, whereas under similar conditions practically the whole of the ethylpyrrolidine undergoes rupture. Somewhat similar results are obtained when the corresponding propyl derivatives are used. The pyrrolidine ring is thus more readily formed and also more readily ruptured than the piperidine ring, and according to Harries (*Annalen*, 1910, **374**, 288), *cyclo*pentene is more readily ruptured than *cyclo*hexene.

1-*Propylpyrrolidine*, C_4NH_8Pr, obtained by the action of *n*-propylamine on $\alpha\delta$-di-iodobutane, is a mobile liquid with b. p. 130°. It is readily soluble in water, and has an intense basic odour. The *picrate*, $C_{13}H_{13}O_7N_4$, crystallises in yellow plates, m. p. 105°, and the *platinichloride*, $C_{14}H_{32}N_2Cl_6Pt$, forms red crystals, which begin to turn black at 184°, and are completely decomposed at 190°. The product obtained by the action of cyanogen bromide cannot be distilled, but after treatment with piperidine, it yields *pentamethylenecyanopropylputrescine*, $C_5NH_{10}\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NPr^{\alpha}\cdot CN$, as a viscid, colourless liquid, b. p. 191—192°/16 mm. Its salts are oily, and the base is comparatively stable, but when heated for twelve hours at 155° with fuming hydrochloric acid yields *α-piperidino-δ-*n*-propylaminobutane* (*pentamethylenepropylputrescine*),

$$C_5NH_{10}\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NHPr,$$

as a mobile liquid, b. p. 130°/10 mm. The *picrate*,

$$C_{12}H_{26}N_2,2C_6H_3O_7N_3,$$

has m. p. 139—140°, and the *platinichloride*, $C_{12}H_{28}N_2Cl_6Pt$, crystallises in yellow plates, m. p. 217° (decomp.).

1-*Ethylpyrrolidine*, $C_6H_{13}N$, has b. p. 106°; the *picrate*, $C_{12}H_{16}O_7N_4$, crystallises in glistening plates, m. p. 185°, and the *platinichloride* does not crystallise well. *Pentamethylenecyanoethylputrescine*,

$$C_5NH_{10}\cdot[CH_2]_4\cdot NEt\cdot CN,$$

has b. p. 182°/16 mm., and *pentamethylene-ethylputrescine* (*α-piperidino-δ-ethylaminobutane*), $C_5NH_{10}\cdot[CH_2]_4\cdot NHEt$, b. p. 125—126°/13 mm. The *picrate*, $C_{11}H_{24}N_2,2C_6H_3O_7N_3$, forms a fine yellow powder, m. p. 113°, and the *platinichloride*, $C_{11}H_{26}N_2Cl_6Pt$, has m. p. 216—217° (decomp.).

When tropan is treated with cyanogen bromide in ethereal solution, a small amount of methyl bromide is eliminated, but the chief product is a quaternary ammonium salt insoluble in ether. It is highly probable that this salt is formed by the rupture of the ring and the formation of a brominated cyanamide, $CN\cdot NMe\cdot CH{<}\begin{matrix} CH_2\cdot CH_2\cdot CH_2 \\ CH_2\cdot CH_2\cdot CHBr \end{matrix}$,

which combines with the excess of tropan, yielding the quaternary salt. The other product, *cyanonortropan*, has b. p. 148—150°/17 mm. and m. p. 108° (annexed formula), and on hydrolysis yields nortropan (Ladenburg, Abstr., 1887, 740). Cyanotropan, when heated at 150° with an excess of aniline hydrochloride and then distilled in steam, yields s-*nortropylphenylguanidine*, $C_7H_{12}N\cdot C(:NH)\cdot NHPh$, which crystallises from aqueous alcohol in glistening needles, m. p. 145°. The *picrate* has m. p. 157—158°, and the *platinichloride* decomposes at 208°.

$$\begin{array}{l} CH_2\cdot CH\cdot CH_2 \\ |\quad\; N\cdot CN \quad\quad > CH_2 \\ CH_2\cdot CH\cdot CH_2 \end{array}$$

J. J. S.

Syntheses of Pyrrole Compounds from Imino-acids. *N*-Phenyl-$\alpha\alpha'$-dicarbethoxy-$\beta\beta'$-diketopyrrolidine [Ethyl 3 : 4-Diketo-1-phenylpyrrolidine-2 : 5-dicarboxylate]. TREAT B. JOHNSON and ROBERT BENGIS (*J. Amer. Chem. Soc.*, 1911, **33**, 745—755).—It has been shown by Johnson and Johns (Abstr., 1906, i, 874) that ethyl oxalate condenses with ethyl diglycollate with formation of ethyl 3 : 4-diketotetrahydrofuran-2 : 5-dicarboxylate. In continuation of this work, a study has now been made of the condensation of ethyl oxalate with ethyl phenylglycinoacetate.

Mouilpied (Trans., 1905, **87**, 435) has found that ethyl oxalate condenses with ethyl phenylglycinoacetate in presence of sodium ethoxide to form a compound, $C_{16}H_{17}O_6N$, m. p. 137°, to which he was unable to assign a satisfactory constitutional formula, but regarded it as having a quinonoid structure, as it yields a yellow sodium salt. A re-investigation of this substance has shown that it is ethyl 3 : 4-diketo-1-phenylpyrrolidine-2 : 5-dicarboxylate, $NPh<\begin{array}{l}CH(CO_2Et)\cdot CO\\ CH(CO_2Et)\cdot CO\end{array}$. This compound gives a yellow di-sodium salt and a colourless *mono-sodium* salt; the *barium* salt crystallises with $1H_2O$.

When the yellow sodium salt is heated with *p*-nitrobenzyl chloride in presence of alcohol, a small quantity of *ethyl* 3 : 4-*diketo*-1-*phenyl*-2-p-*nitrobenzylpyrrolidine*-2 : 5-*dicarboxylate*,

$$NPh<\begin{array}{l}C(CO_2Et)(CH\cdot C_6H_4\cdot NO_2)\cdot CO\\ CH(CO_2Et)\text{————————}CO\end{array},$$

m. p. 180—182° (decomp.), is obtained as an orange-coloured powder. The main product of the reaction, however, is *ethyl* 3 : 4-*diketo*-1-*phenyl*-2 : 5-*di*-p-*nitrobenzylpyrrolidine*-2 : 5-*dicarboxylate*,

$$NPh<\begin{array}{l}C(CO_2Et)(CH\cdot C_6H_4\cdot NO_2)\cdot CO\\ C(CO_2Et)(CH\cdot C_6H_4\cdot NO_2)\cdot CO\end{array} \text{ or }$$

$$NPh<\begin{array}{l}C(CO_2Et)(CH\cdot C_6H_4\cdot NO_2)\cdot CO\\ C(CO_2Et)\text{=========}C\cdot O\cdot CH_2\cdot C_6H_4\cdot NO_2\end{array},$$

m. p. 132°, which forms yellow prisms.

Attempts to reduce ethyl 3 : 4-diketo-1-phenylpyrrolidine-2 : 5-dicarboxylate with hydriodic acid and also with aluminium amalgam were not successful.

Mouilpied (*loc. cit.*) observed that if the condensation of ethyl oxalate with ethyl phenylglycinoacetate is effected in presence of sodium methoxide instead of the ethoxide, the ethyl ester, m. p. 137°, is not produced, but the corresponding methyl ester, m. p. 188°, is

formed. He therefore carried out the several condensations of methyl and ethyl oxalates with methyl and ethyl phenylglycinoacetates in presence of sodium methoxide and of sodium ethoxide. From these eight condensations, he obtained six different compounds. These experiments have now been repeated, and it has been found that only two compounds are actually produced. The compound, m. p. 137°, is formed by the condensation of ethyl or methyl oxalate with ethyl or methyl phenylglycinoacetate in presence of sodium ethoxide, whilst by the condensation of these esters in presence of sodium methoxide, the compound, m. p. 188—189°, is obtained. It is evident, therefore, that the product of the reaction is determined by the particular alkyloxide used. The compound, m. p. 188—189°, is methyl 3 : 4-diketo-1-phenylpyrrolidine-2 : 5-dicarboxylate. E. G.

Pyridinoiridopentachlorides. MARCEL DELÉPINE (*Compt. rend.*, 1911, 152, 1390—1393. Compare Abstr., 1908, ii, 702; 1910, ii, 44).—The metallic pyridinoiridopentachlorides are formed by introducing a molecule of pyridine into an aquoiridopentachloride in place of $1H_2O$, or into an alkali iridohexachloride in place of a molecule of alkali chloride.

Potassium, sodium, and *ammonium pyridinoiridopentachlorides* conform to the type $IrCl_5(C_5H_5N)M_2$, and are best prepared by treating a hot solution of the iridochloride with excess of pyridine and removing the excess as rapidly as possible. The products vary in colour from orange to red according to the size of the crystals. The *thallium, silver, mercurous,* and *mercuric* salts are amorphous and insoluble in water. Orange crystals having the composition $IrCl_5(C_5H_5N)(NH_3Ag)_2,H_2O$ are obtained when the silver salt is dissolved in ammonia. The alkali salts are very stable, and the pyridine is not removed by concentrated sulphuric acid at 100°. Chromic acid and hydrogen peroxide are without action, but chlorine and nitric acid convert them into a new series of salts of the type $IrCl_5(C_5H_5N)M$. W. O. W.

Pyridinoiridipentachlorides. MARCEL DELÉPINE (*Compt. rend.*, 1911, 152, 1589—1591. Compare preceding abstract).—The pyridinoiridipentachlorides of the type $IrCl_5(C_5H_5N)M$ are related to the pyridinoiridopentachlorides previously described, in the same way as the iridihexachlorides are to the iridohexachlorides. They are best obtained by the action of nitric acid on the corresponding pyridinoiridopentachlorides. The *potassium, ammonium, rubidium, caesium,* and *sodium* salts form very deep red crystals, and are anhydrous except in the last case. Like the pyridinoiridopentachlorides they give precipitates with aqueous solutions of thallium, silver, mercurous, and mercuric salts, but differ from them in giving no precipitate with lead salts. The *silver* salt crystallises in slender, violet needles.

These salts are remarkably stable towards acids, but lose pyridine when heated with hydrochloric acid in sealed tubes at 150—160°, giving the corresponding hexachlorides. W. O. W.

Pyridylacetylcatechol and Related Bases. CARL MANNICH and O. HÜBNER (*Ber. Deut. pharm. Ges.*, 1911, 21, 294—297. Compare Abstr., 1910, i, 411).—A number of bases somewhat similar in structure to

adrenaline have been prepared by condensing pyridine, piperidine, or quinoline with chloroacetylcatechol or the bromoacetyl derivative of catechol dimethyl ether.

Chloroacetylcatechol, $C_6H_3(OH)_2 \cdot CO \cdot CH_2Cl$, condenses with pyridine when gently warmed with it in alcohol to form *pyridylacetylcatechol hydrochloride*, $C_6H_3(HO)_2 \cdot CO \cdot CH_2 \cdot C_5NH_5Cl$, m. p. 272° (decomp.). which crystallises from hot water, and on addition of ammonia yields the free *base* (or pseudo-base), m. p. 199° (decomp.), in the form of yellow crystals. *Pyridylacetylveratrole hydrobromide*,

$$C_6H_3(OMe)_2 \cdot CO \cdot CH_2 \cdot C_5NH_5Br,$$

m. p. 258° (decomp.), similarly obtained, also crystallises from hot water, but the free base could not be isolated by the action of alkalis. When heated with hydrochloric acid, the methoxyl groups were eliminated and pyridylacetylcatechol hydrochloride was formed.

Piperidylacetylcatechol hydrochloride, m. p. 257° (decomp.), forms colourless needles from water; the free *base*, m. p. 199—205° (decomp.), is liberated from the hydrochloride by ammonia. *Quinolylacetylveratrole hydrobromide*, $C_6H_3(OMe)_2 \cdot CO \cdot CH_2 \cdot C_9NH_7Br$, m. p. 222° (decomp.), crystallises from hot water. With ammonia it furnishes a reddish-brown, amorphous *product*, and when heated with hydrochloric acid yields a *product*, $C_{17}H_{14}O_3NCl$, m. p. 248° (decomp.), which separates from water in yellowish-brown crystals and gives catechol reactions. The free base could not be obtained. Quinoline does not condense directly with chloroacetylcatechol. T. A. H.

New Oxidation of 2-Methylindole. GIUSEPPE PLANCHER and U. COLACICCHI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 453—457).—With the exception of fusion with potassium hydroxide, all methods previously used for the oxidation of 2-methylindole result in the rupture of the nucleus and the formation of anthranilic acid and its substitution products.

Oxidation of 2-methylindole by means of 15% ethereal hydrogen peroxide solution yields, however, the *compound*,

$$NH{<}{}^{C_6H_4}_{CMe}{\geqslant}C \cdot O \cdot C{\leqslant}{}^{C_6H_4}_{CMe}{>}NH$$

or $CH{\leqslant}{}^{CMe}_{C_6H_4}{>}N \cdot O \cdot N{<}{}^{CMe}_{C_6H_4}{\geqslant}CH$, which forms greenish-yellow crystals, m. p. 209—210°, and has the normal molecular weight in freezing naphthalene. It gives a red coloration with boiling acetic acid, whilst with concentrated sulphuric acid it yields a blue solution, which becomes green and deposits green flocks on dilution with water. On reduction with tin and hydrochloric acid, it gives dihydro-2-methylindole.

The same product is formed from 2-methylindole by oxidation with aqueous hydrogen peroxide or Caro's acid, and together with other compounds, not yet studied, with ozone in presence of water or chloroform.

Attempts to oxidise 2-phenylindole and 2 : 3-dimethylindole by means of hydrogen peroxide have as yet led to no definite results.

T. H. P.

8-Hydroxyquinoline. GEORG COHN (*J. pr. Chem.*, 1911, [ii], 83, 498—506).—8-Hydroxyquinoline and formaldehyde, which yield hydroxymethyl-8-hydroxyquinoline under Manasse's conditions (Abstr. 1903, i, 28), produce another substance, called "*new hydroxyquinoline-carbinol*," when a mixture of 5 grams of 8-hydroxyquinoline, 15 c.c. of formalin, and 10 c.c. of 20% sodium hydroxide are heated on the water-bath; by dilution with water and neutralising with hydrochloric or acetic acid, the new compound, $C_{12}H_9O_2N$, is obtained as a yellow, amorphous powder. It does not melt at 250°, evolves formaldehyde at higher temperatures, forms a solution in dilute hydrochloric acid which is coloured dark green by ferric chloride, yields a yellow sodium salt, couples with diazobenzenesulphonic acid, and is oxidised by alkaline potassium ferricyanide to a dark green substance.

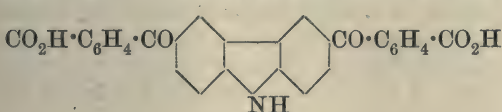
8-Hydroxyquinoline-5-sulphonic acid is formed when loretin (7-iodo-8-hydroxyquinoline-5-sulphonic acid) is boiled with water and aniline or phenetidine, with piperidine, or with guaiacol and sodium hydroxide.

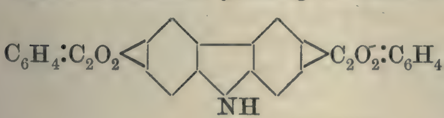
5-Nitroso-8-hydroxyquinoline is reduced by phenylhydrazine on the water-bath, yielding 5-*azo*-8-*hydroxyquinoline*,

$$OH\cdot C_9NH_5\cdot N:N\cdot C_9NH_5\cdot OH,$$

m. p. 220° (decomp.), brownish-red needles with a blue reflex. By reduction with potassium sulphite the nitroso-compound yields a substance, not yet fully examined, which is probably an amino-hydroxyquinolinesulphonic acid. C. S.

Introduction of Several Phthalic Acid Groups into Aromatic Compounds. IV. Experiments with Carbazole. ROLAND SCHOLL and WERNER NEOVIUS (*Ber.*, 1911, 44, 1249—1252. Compare this vol., i, 452, 453, 557).—Carbazole reacts with phthalic anhydride and aluminium chloride, either with or without a diluent, yielding *carbazole*-3 : 6-*diphthaloylic acid* (I.), and this reacts with concentrated sulphuric acid at 90° and then at 100°, yielding 2 : 3 : 6 : 7-*diphthaloylcarbazole* (II.). In the preparation of the dibasic acid a certain amount of the *N*-phthaloylic acid (carbazole-*N*-carbonyl-*o*-benzoic acid: Stummer, Abstr., 1907, i, 723) is formed, and can be removed by hydrolysis with sodium hydroxide, and also a certain amount of the 3-phthaloylic acid, which is removed by adding a small amount of magnesium sulphate to the solution of the ammonium salts. The dibasic acid, $C_{28}H_{17}O_6N$, forms a colourless, amorphous powder, m. p. 300—301°.


(I.)


(II.)

2 : 3 : 6 : 7-*Diphthaloylcarbazole*, $C_{28}H_{13}O_4N$ (II.), crystallises from quinoline in golden-yellow needles, which are not molten at 450°. With alkaline hyposulphite solutions, it yields a dark brown vat-dye.

J. J. S.

Oximes and Phenylalkyl*iso*oxazolones Obtained from Ethyl Benzoylpropionate, Benzoyl-*n*-butyrate, and Benzoyl*iso*butyrate. ALBIN HALLER and EDMOND BAUER (*Compt. rend.*, 1911, **152**, 1446—1450. Compare this vol., i, 299).—The substance, m. p. 91°, obtained by Hantzsch and Miolati (Abstr., 1893, 583) by acting on ethyl benzoyl-*n*-butyrate with hydroxylamine hydrochloride and potassium hydroxide gives analytical results indicating it to be *phenylethyl*isoo*xazolone*, and not an oxime, as these authors supposed. The corresponding *oxime*, however, is formed when the ester is treated with hydroxylamine zincochloride in alcoholic solution, and occurs in prisms, m. p. 80—81°. Similar results were obtained with alkyl derivatives of ethyl benzoylacetate, Crismer's reagent always leading to the production of an oxime, and hydroxylamine to that of a phenyl*iso*oxazolone. The latter is also formed by withdrawing $1H_2O$ from the oxime.

*Phenylmethyl*isoo*xazolone*, $C_{10}H_9O_2N$, has m. p. 123—124°; *phenyldimethyl*isoo*xazolone*, $CMe_2<\begin{matrix}CPh\\O\cdot CO\end{matrix}>N$, has m. p. 70—71°.

W. O. W.

The Simplest Quinonoid Dyes. JEAN PICCARD (*Annalen*, 1911, **381**, 351—366).—The *meri*quinonedi-imonium salts,

$$NH_2Br\!:\!C_6H_4\!:\!NH_2Br\!:::\!NH_2\cdot C_6H_4\cdot NH_2,$$

and their methyl derivatives exist in α- and β-modifications (compare Abstr., 1910, i, 66). The α-compounds exhibit characteristic absorption spectra, all of much the same type, although the colour of the solutions passes from yellow through orange, red, and violet to blue with an increase in the number of methyl groups present. The more strongly coloured salts, the β-modifications, are most readily obtained at low temperatures, especially in the presence of water, whereas alcohol favours the formation of the α-compounds. The solutions, as a rule, consist of equilibrated mixtures, but the equilibrium can be appreciably altered by changing the conditions. The imonium salt itself and its mono- and di-methyl derivatives exist in the solid state as the β-forms only, whereas the tri- and tetra-methyl derivatives exist as the solid α-forms. The absorption spectra of the β-modifications are essentially different from those of the α, and do not consist of a number of characteristic bands. By the use of the colorimetric dilution law (this vol., ii, 561,) it is shown that the α- and β-modifications are not isomeric, but polymeric, and the conversion of the β- into the α-form consists in depolymerisation or dissociation.

The rate of transformation is extremely rapid, so that a given salt does not exist in both forms under given specific conditions. The α-form of the *meri*quinonedi-imonium bromide exists only in dilute solution at 0°; under all other conditions the β-form is the stable form, but with the tetramethyl derivative the α-form is the only one which has been observed either in the solid state or in solution.

As a rule, the β- are more stable than the α-compounds. *meri*-Quinonedi-imonium bromide (compare Jackson and Calhane, Abstr., 1902, i, 645; Pringsheim, *ibid.*, 1905, i, 934; Kehrmann, *ibid.*, 1906, i, 46) crystallises as a heavy, brown powder with a golden-yellow

lustre when it is deposited gradually from a mixture of alcohol and glacial acetic acid. The corresponding *nitrate*, $C_{12}H_{16}O_6N_6$, has a brassy lustre. The meri*methylquinonedi-imonium bromide*,

$$C_{14}H_{20}N_4Br_2,$$

is amorphous. meri*Trimethylquinonedi-imonium ferricyanide*,

$$NHMe\cdot C_6H_4\cdot NMe_2,HFeC_6N_6,2NHMe\cdot C_6H_4\cdot NMe_2,$$

crystallises in brilliant black needles. J. J. S.

Aromatic Hydrazines. IX. Tetraphenylhydrazine and Hexaphenylethane. HEINRICH WIELAND (*Annalen*, 1911, **381**, 200—216).—Tetra-arylated hydrazines are readily hydrolysed to diarylated amines and diarylated hydroxylamines, but as the latter are unstable they cannot be directly isolated, but are transformed into decomposition or condensation products (compare Abstr., 1906, i, 830; 1907, i, 1076; 1908, i, 1014, 1026; this vol., i, 83).

It is now shown that tetraphenylhydrazine is partly depolmerised (dissociated) when boiled with toluene, and thus resembles hexaphenylethane, which is partly dissociated into triphenylmethyl in benzene solution. It has not been found possible to isolate the primary dissociation product, $-NPh_2$, as this is extremely unstable and undergoes further transformation.

[With HANS LECHER.]—When the toluene solution of tetraphenylhydrazine is boiled, a green colour is developed, but this changes rapidly to brown, and on cooling the colour does not disappear. After boiling for thirty minutes, removing the toluene under reduced pressure, and then adding ether, crystals of diphenyldihydrophenazine are obtained, and diphenylamine and *o*-anilinotriphenylamine remain in solution. Details for the separation of the three compounds are given. The diphenylamine and diphenyldihydrophenazine are regarded as being formed by the reduction of one portion of the dissociation product at the expense of the other:

$$2-N{<}{}^{C_6H_5}_{C_6H_5} + 2-N{<}{}^{C_6H_5}_{C_6H_5} = 2H\cdot N{<}{}^{C_6H_5}_{C_6H_5} + C_6H_4{<}{}^{NPh}_{NPh}{>}C_6H_4.$$

This reaction is analogous to the formation of triphenylmethane and a complex bimolecular hydrocarbon from triphenylmethyl. The formation of *o*-anilinotriphenylamine [triphenyl-*o*-phenylenediamine], $NHPh\cdot C_6H_4\cdot NPh_2$, from tetraphenylhydrazine is due to a semidine transformation, and is analogous to the formation of benzhydryltetraphenylmethane from hexaphenylethane, except that in the latter case the substituents occupy the para-position.

Diphenyldihydrophenazine, $C_{24}H_{18}N_2$, crystallises from a mixture of benzene and alcohol in colourless needles, m. p. 172—175°. On exposure to the air it turns green, as it is readily oxidised to a *o*-quinonoid salt. Its benzene solutions have more or less colloidal properties, and with bromine it yields a *bromide*,

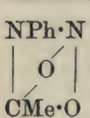
$$C_6H_4{<}{}^{NPhBr}_{NPhBr}{\geqslant}C_6H_4,$$

the chloroform solutions of which have a brilliant green colour.

Triphenyl-o-phenylenediamine, $C_{24}H_{20}N_2$, is amorphous, has m. p. 85°, and yields a crystalline *hydrochloride*. The base reacts with bromine, evolving hydrogen bromide and yielding diphenyldihydrophenazine

dibromide. The blue compound obtained by treating diphenylamine with concentrated sulphuric acid and an oxidising agent is shown to be identical with the *o*-quinonoid sulphate of diphenyldihydrophenazine, $C_6H_4 < \substack{NPh(O\cdot SO_3H) \\ NPh(O\cdot SO_3H)} \gg C_6H_4$, and its formation is due to the following series of reactions. Oxidation of diphenylamine to tetraphenylhydrazine, hydrolysis of the latter to diphenylamine and diphenylhydroxylamine, and condensation of the hydroxylamine to diphenyldihydrophenazine (phenoperazine), and, finally, oxidation of this to the *o*-quinonoid salt.

The dissociation of tetraphenylhydrazine can also be shown by passing nitric oxide into a toluene solution of the hydrazine, heated at 90—95° and protected from atmospheric oxygen. After some twenty to thirty minutes the hydrazine is transformed quantitatively into diphenylnitrosoamine. The nitrosoamine when heated at 130° gives a theoretical yield of nitric oxide, showing that the reaction is reversible. The other products are diphenylamine and diphenyldihydrophenazine, although the amount of the latter is very small. Di-*p*-tolylnitrosoamine and di-*p*-anisylnitrosoamine behave in a similar manner. Nitrosoarylamides behave in quite a different manner (Bamberger, Abstr., 1894, i, 412; 1910, i, 908); when heated in an indifferent solvent, for example, light petroleum, they explode or evolve nitrogen, but not nitric oxide. The annexed structural formula is suggested for these compounds.



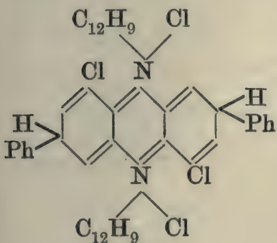
When triphenylmethyl is heated on the water-bath with a toluene solution of tetraphenylhydrazine in the absence of air, crystals of *triphenylmethyldiphenylamine*, $CPh_3\cdot NPh_2$, are obtained. The formation of this compound is due to the union of the two unsaturated groups, CPh_3- and $-NPh_2$. It forms large, colourless, transparent needles, m. p. 172°, and with concentrated sulphuric acid yields triphenylcarbinol and diphenylamine. In boiling xylene the compound is partly dissociated the solution has a red colour, and gives all the characteristic reactions of triphenylmethyl. *Triphenylmethyldi*-p-*tolylamine*, $C_{33}H_{29}N$, has m. p. 164°, and, like the diphenylamine derivative, gives a red melt.

Tetraphenyl-, di-*p*-tolyl-, and di-*p*-anisyl- hydrazines give a blue phosphorescence when subjected to the action of cathode rays, and themselves turn green in the course of a few seconds. Tetratolylhydrazine and *p*-tetradiphenylhydrazine are coloured dark yellow, but these colours disappear rapidly when the substances are removed from the influence of the cathode rays. J. J. S.

Aromatic Hydrazines. X. Tetradiphenylhydrazine. HEINRICH WIELAND and ARTHUR SÜSSER (*Annalen*, 1910, 381, 217—229. Compare preceding abstract).—Tetradiphenylhydrazine is not dissociated so readily as tetraphenylhydrazine, and its properties resemble tetra-*p*-tolyl- rather than tetraphenyl-hydrazine. It is prepared by oxidising an acetone solution of *p*-didiphenylamine with finely-powdered permanganate at 10°. p-*Didiphenylamine*, $NH(C_{12}H_9)_2$, can be obtained as its acetyl derivative by boiling *p*-iododiphenyl and *p*-acetylaminodiphenyl, potassium carbonate, copper bronze, a

little iodine, and potassium iodide with nitrobenzene for twenty-four hours. The base, obtained by hydrolysing the acetyl derivative with alcoholic potassium hydroxide, crystallises from benzene or xylene in glistening, nacreous plates, m. p. 209°. The *hydrochloride* forms long prisms; the *nitrosoamine*, $C_{24}H_{18}ON_2$, crystallises from benzene in yellow needles, m. p. 172°.

Tetradiphenylhydrazine, $N_2(C_6H_4Ph)_4$, crystallises slowly from a mixture of benzene and alcohol, has m. p. 165°, and, when warmed with glacial acetic acid, gives a characteristic intense violet coloration. When boiled for some time in xylene solution, dissociation can be recognised by the separation of the sparingly soluble didiphenylamine. *Didiphenyldihydrophenazine*, $C_{48}H_{34}N_2$, does not appear to be formed, but was met with in the mother liquors from the hydrazine after they had been kept for several months. It crystallises from xylene in yellow needles, m. p. 325—330°, and yields a *hydrochloride* in the form of broad, violet needles, with a quinonoid constitution.



(I.)

The hydrazine combines with hydrogen chloride in the presence of benzene, light petroleum, and ether, yielding a flocculent, green *hydrochloride*, $C_{48}H_{36}N_2,2HCl$, which is gradually transformed into didiphenylamine hydrochloride, the violet *chloride* of *dichlorodiphenoperazine*, together with an isomeride of the tetra-arylated hydrazine and *o*-chlorodiphenylamine. The violet chloride (I), when treated with a little ammonia or alcoholic potassium hydroxide, yields *dichlorodiphenoperazine*,

$$C_6H_2PhCl{<}{\genfrac{}{}{0pt}{}{N(C_6H_4Ph)}{N(C_6H_4Ph)}}{>}C_6H_2PhCl\,;$$

this crystallises from xylene in yellow needles, which are not molten at 380°. When reduced with sodium and amyl alcohol in the presence of xylene the dichloro-derivative yields didiphenyldihydrophenazine (diphenoperazine). The isomeride of the hydrazine is probably *o-diphenylaminotridiphenylamine*, $C_6H_4Ph{\cdot}NH{\cdot}C_6H_3Ph{\cdot}N(C_6H_4Ph)_2$; it crystallises from hot xylene in felted needles, m. p. 275°, and gives a green coloration with ferric chloride or with bromine.

o-Chlorodidiphenylamine, $C_{24}H_{18}NCl$, crystallises from alcohol, melts to a turbid liquid at 119°, and becomes clear at 130°.

Tetradiphenylhydrazine and bromine yield an unstable, dark green bromide, which is rapidly decomposed, yielding didiphenylamine and *dibromodidiphenylamine*, $C_{24}H_{17}NBr_2$, in the form of long, glistening needles, m. p. 151°. J. J. S.

The Stability of the Nitrogen Linking in Ketazines. HEINRICH WIELAND and A. ROSEEU (*Annalen*, 1911, 381, 229—233).—According to Curtius and his pupils, the ketazines which contain a grouping similar to nitric oxide (bimolecular form), O:N·N:O and $R_2C{:}N{\cdot}N{:}CR_2$, are extremely stable and do not dissociate. The ketazines derived from the following ketones have been prepared and

examined: benzophenone, fluorenone, and tetramethyldiaminobenzophenone. All the compounds are stable, they dissolve in concentrated sulphuric acid without decomposition, can be distilled to a certain extent without decomposition, and when hydrolysed by hot mineral acids yield hydrazine and ketone.

Benzophenoneketazine (Curtius and Rauterberg, *J. pr. Chem.*, 1901, 63, 94) is quite colourless, but its solutions have a yellow colour, and the intensity of the colour in different solvents increases in the order: Ethyl alcohol, ether, acetone, benzene, chloroform. It yields an unstable lemon-yellow hydrochloride and a reddish-orange bromide.

Fluorenonehydrazone, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>C:N\cdot NH_2$, is formed when the ketone and hydrazine hydrate are warmed with a little alcohol on the water-bath, and crystallises from alcohol in pale yellow plates, m. p. 149°. When oxidised with the theoretical amount of iodine in alcoholic solution, it yields *fluorenoneketazine*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>C:N\cdot N\cdot C<\!\!\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}$, and nitrogen. The ketazine crystallises from xylene in brilliant dark red needles, m. p. 259°, and its solution in concentrated sulphuric acid has a purple-red colour. When reduced with zinc dust and glacial acetic acid it yields 9-aminofluorene.

Tetramethyl-p-*diaminodiphenylketone hydrazone*,

$$C(C_6H_4\cdot NMe_2)_2:N\cdot NH_2,$$

obtained by heating the components with a little alcohol at 180°, crystallises from alcohol in pale yellow needles, m. p. 150°. The *benzylidene* derivative, $C_{24}H_{26}N_4$, crystallises from alcohol in pale orange-yellow needles, m. p. 141°, and the *ketazine*,

$$C(C_6H_4\cdot NMe_2)_2:N\cdot N:C(C_6H_4\cdot NMe_2)_2,$$

obtained by oxidising the hydrazone with mercuric oxide and a little iodine, crystallises from xylene in large, brownish-red prisms, m. p. 253°. Its solution in concentrated sulphuric acid is practically colourless.

J. J. S.

Preparation of 5:5-dialkyliminobarbituric Acid (2-Imino-4:6-diketo-5:5-dialkylpyrimidine). EMANUEL MERCK (D.R.-P. 231887).—When 5:5-dialkylmalonic acid diaryl esters are heated with guanidine (or a guanidine salt), they yield imino-5:5-dialkylbarbituric acids. 2-Iminodiethylbarbituric acid, prepared by heating diphenyl diethylmalonate with guanidine carbonate at 160°, may subsequently be converted into diethylbarbituric acid. F. M. G. M.

Relationships between Perbromides and Bromo-substitution Products Observed with Acetylacetonecarbamide [4:6-Dimethyl-2-pyrimidone] and its Tautomeride. OTTO STARK (*Annalen*, 1911, 381, 143—199).—Evans's acetylacetonecarbamide [4:6-dimethyl-2-pyrimidone] (Abstr., 1893, i, 129; 1894, i, 111; Stark, 1909, i, 259) combines with two or with four atoms of bromine, yielding products which are regarded as perbromides and not as compounds formed by the addition of bromine to unsaturated linkings, since the bromine is not firmly attached to the molecule. As pyridine and quinoline also yield perbromides, it is suggested that the bromine

combines with the nitrogen atoms of the molecule, and the following formulæ are given to the di- and tetra-bromide:

$$CO<{N{=\!=}CMe \atop NBr_2{:}CMe}>CH_2 \text{ and } CO<{NBr_2{:}CMe \atop NBr_2{:}CMe}>CH_2.$$

To distinguish the two tautomeric forms, the name acetylacetonecarbamide will be used in this abstract for the original compound and 4 : 6-dimethyl-2-pyrimidone for its isomeride. The latter also yields perbromides, and these with water or alcohol yield the same products as are obtained from the perbromide of the carbamide. The two sets of perbromides are not regarded as being identical, since the one from the pyrimidone loses its colour more rapidly than that derived from the carbamide.

The perbromide of acetylacetonecarbamide, $C_6H_8ON_2Br_2$, can be obtained by the addition of bromine to a chloroform solution of the carbamide (Abstr., 1909, i, 259), or to a solution of the carbamide in hydrobromic acid (b. p. 121°). In the latter case orange-yellow needles are obtained, which darken in colour when heated, but have no definite m. p. When triturated with water, it yields a pentabromide, $C_6H_7ON_2Br_5$, Evans's dibromodihydroxy-derivative (5-dibromo-4 : 6-dihydroxy-4 : 6-dimethyl-2-tetrahydropyrimidone), and 5-bromo-4 : 6-dimethyl-2-pyrimidone.

The last compound is contained in the aqueous liquid, and can be isolated as its sodium derivative. The first two compounds are present in the colourless solid, and after this has been dried the pentabromo-derivative can be extracted by chloroform.

5-Dibromo-4 : 6-dihydroxy-4 : 6-dimethyl-2-tetrahydropyrimidone, $CO<{NH{\cdot}CMe(OH) \atop NH{\cdot}CMe(OH)}>CBr_2$, is sparingly soluble in most solvents; its solubility in ethyl alcohol is 1 in 100, but at the same time it undergoes partial decomposition, yielding a dye, which crystallises in deep violet prisms.

The same decomposition occurs when the compound is boiled or kept some time in contact with water, and also when the solid is heated for some time at 100°. With carbon disulphide, the dihydroxy-derivative forms a gelatinous mass, which crystallises on the addition of a solvent miscible with carbon disulphide. It dissolves in cold sodium hydroxide solution (4 mols.), and when acidified after two to three hours yields carbon dioxide, acetic and lactic acids, ammonia, and hydrobromic acid. It is claimed that the formation of these products is more in harmony with the author's view of the constitution of the dihydroxy-derivative than with Evans's view.

Colourless anhydrous 4 : 6-dimethyl-2-pyrimidone is obtained when anhydrous acetylacetonecarbamide is dissolved in absolute alcohol, mixed with the theoretical amount of sodium ethoxide, the precipitated sodium derivative removed, dried, suspended in absolute alcohol, and dry carbon dioxide passed in. The filtered solution is evaporated to dryness at the ordinary temperature over potassium hydroxide and concentrated sulphuric acid, and the residue crystallised from acetone, when the pyrimidone is obtained as colourless, glistening needles, m. p. 200°.

Acetylacetonecarbamide perbromide, $C_6H_8ON_2Br_4$, obtained from

either chloroform or distilled hydrobromic acid solution, forms red, microscopic needles; it has no definite m. p., it changes colour at 150° to 160°, and is completely decomposed at 220°. With water it yields 5-dibromo-4 : 6-dihydroxy-4 : 6-dimethyl-2-tetrahydropyrimidone and 5-bromo-4 : 6-dimethyl-2-pyrimidone.

By the action of a solution of bromine in dilute acetic acid on a glacial acetic acid solution of acetylacetonecarbamide at 30—40° it has not been found possible to obtain the bromohydroxy-derivative previously described (*loc. cit.*); the only product obtained was the *hydrobromide* of the carbamide, $C_6H_8ON_2,HBr$. The same product was also obtained by the action of alcohol on the perbromide of the carbamide, and by dissolving the carbamide in a mixture of glacial acetic acid and concentrated hydrobromic acid. It crystallises from alcohol in colourless needles, which decompose at 345° after changing colour at 240—250°.

An aqueous solution of sodium hypobromite reacts with acetylacetonecarbamide, yielding the *sodium* salt of 5-bromo-4 : 6-dimethyl-2-pyrimidone, in the form of slender, colourless needles, decomposing rapidly at 336—338°. The corresponding hydrogen compound exists in two forms. *Bromoacetylacetonecarbamide*,

$$CO{<}{\begin{matrix}N{:}CMe\\N{:}CMe\end{matrix}}{>}CHBr,$$

obtained by the action of acetic acid on the sodium salt, crystallises in pale yellow needles or prisms, and decomposes at 228—231°. 5-*Bromo*-4 : 6-*dimethyl*-2-*pyrimidone*, $CO{<}{\begin{matrix}NH\cdot CMe\\N{=}CMe\end{matrix}}{>}CBr$, obtained by boiling the sodium salt and the theoretical amount of acetic acid, crystallises in colourless needles or in colourless, glistening prisms. The yellow compound can be transformed into the colourless by boiling with water and adding a few drops of concentrated ammonium hydroxide solution, and can be transferred back into the yellow modification by boiling with dilute acetic acid. The monobromo-derivative yields a colourless *nitrate*, $C_6H_7ON_2Br,HNO_3$, in the form of glistening needles, which decompose between 160° and 200°; it also yields a reddish-yellow *dinitrate*, $C_6H_7ON_2Br,2HNO_3,3H_2O$, which explodes at about 196—197°.

The *perbromide* of bromoacetylacetonecarbamide, $C_6H_7ON_2Br,Br_2$, forms chrome-yellow needles, decomposes at 160—200°, and with water yields 5-dibromo-4 : 6-dihydroxy-4 : 6-dimethyltetrahydro-2-pyrimidone. The bromopyrimidone also yields a perbromide with Br_2, but this rapidly becomes colourless when kept.

5 : 5 : 6-*Tribromo*-4 : 6-*dimethyldihydro*-2-*pyrimidone*,

$$CO{<}{\begin{matrix}NH\cdot CMeBr\\N{=\!=}CMe\end{matrix}}{>}CBr_2,$$

obtained by mixing a chloroform solution of 5-bromo-4 : 6-dimethyl-2-pyrimidone with a chloroform solution of bromine at 30—40°, and shaking at the given temperature until hydrogen bromide is evolved, forms colourless crystals, which begin to decompose at 220—240°. It cannot be recrystallised, and when heated with chloroform or treated with water yields *dibromoacetylacetonecarbamide*,

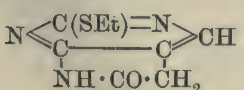
$$CO{<}{\begin{matrix}N{:}CMe\\N{:}CMe\end{matrix}}{>}CBr_2,$$

as colourless needles, decomposing at 160—170°. When water is used, *bromoacetylacetonecarbamide hydrobromide*, $C_6H_8ON_2Br_2$, is also formed. This crystallises from methyl alcohol. The *perbromide* of the monobromo-derivative, $C_6H_7ON_2Br,Br_4$, forms red needles, decomposing between 160° and 200°.

[With P. Horrmann.]—When acetylacetonecarbamide or its monobromo-derivative is brominated in the presence of boiling chloroform, hydrogen bromide is evolved during ten to twelve hours, and the following products are formed: (1) The pentabromide (see above), which remains dissolved in the chloroform; (2) a heptabromide which is insoluble in chloroform, but soluble in benzene; (3) perbromides, insoluble in chloroform and benzene; these on treatment with water yield the dibromodihydroxydimethyldihydropyrimidone and the hydrobromide of bromoacetylacetonecarbamide. The *pentabromide*, probably $CO{<}{\substack{NH\cdot CBr(CH_2Br)\\ NH\cdot CBr(CH_2Br)}}{>}CHBr$, is stable, and crystallises from chloroform or benzene in well-developed, pale yellow prisms, m. p. 183—184° (decomp.). It is not appreciably decomposed when boiled with water for two to three hours, is distinctly acidic, and yields a *sodium* salt, $C_6H_6ON_2Br_5Na$, in the form of slender, colourless needles, which are not decomposed by carbonic acid. It also yields a *hydrobromide* in the form of a yellow, crystalline precipitate, which decomposes when removed from the mother liquor. The *heptabromide*, $C_6H_7ON_2Br_5,Br_2$, crystallises from benzene with partial decomposition in yellow, felted needles, and also tends to give up bromine when kept in a desiccator. It is most readily prepared by the addition of bromine to the pentabromide, and yields the pentabromide by the action of hydroxylic compounds

A table showing the genetic relationships of the different bromo-derivatives is given. J. J. S.

Pyrimidines. LI. Synthesis of Cytosine-5-acetic Acid. Treat B. Johnson [with Harley T. Peck and Joseph A. Ambler] (*J. Amer. Chem. Soc.*, 1911, 33, 758—766).—It has been shown by Johnson and Speh (Abstr., 1907, i, 1083) that ψ-ethylthiocarbamide condenses with the sodium derivative of ethyl formylsuccinate to form ethyl 2-ethylthiol-6-pyrimidone-5-acetate. When this compound is heated with phosphoryl chloride, *ethyl 6-chloro-2-ethylthiolpyrimidine-5-acetate*, $N{<}{\substack{C(SEt)=\!=\!=\!=\!=N\\ CCl\cdot C(CH_2\cdot CO_2Et)}}{>}CH$, b. p. 203—203·5°/16 mm., 215°/28 mm., and 220°/31 mm., is obtained as an oil. If this chloropyrimidine is heated with alcoholic ammonia in a sealed tube at 120—130°, the corresponding amino-compound is not produced, but the γ-*lactam* of *6-amino-2-ethylthiolpyrimidine-5-acetic acid* (*2-ethylthiol-5 : 6-a-pyrrolidone-pyrimidine*) (annexed formula), m. p. 208°, is formed as a red, granular powder, which, on hydrolysis with concentrated hydrochloric acid, is converted into the *hydrochloride* of cytosine-5-acetic acid, which crystallises in minute needles containing $1H_2O$ and decomposes at 135—140°.



Cytosine-5-acetic acid, $N\langle{}^{CO\text{———————}NH}_{C(NH_2)\cdot C(CH_2\cdot CO_2H)}\rangle CH$, forms colourless crystals, and blackens at 240—250°, but does not melt below 290°; it is not precipitated by phosphotungstic acid, mercuric chloride, or copper sulphate, but yields an amorphous precipitate with potassiobismuth iodide; the *picrate*, m. p. 217—218°, crystallises in needles.

Thiocarbamide condenses with ethyl formylsuccinate in presence of sodium ethoxide with formation of ethyl 2-thio-6-pyrimidone-5-acetate, together with a small quantity of another crystalline substance, probably 6 : 6′-*diketo*-2 : 2′-*ethylthiol*-5 : 5′-*dipyrimidine*,

$$SEt\cdot C\langle{}^{NH\cdot CO}_{N—CH}\rangle C\cdot C\langle{}^{CO\cdot NH}_{CH—N}\rangle C\cdot SEt,$$

which decomposes on heating, but has no definite m. p. *Ethyl 2-thio-6-pyrimidone-5-acetate*, $NH\langle{}^{CS\text{——————}NH}_{CO\cdot C(CH_2\cdot CO_2Et)}\rangle CH$, m. p. 178—180°, and the corresponding *acid*, m. p. about 260° (decomp.), form prismatic crystals. E. G.

Pyrimidines. LII. Thiocytosine-5-carboxylic Acid. TREAT B. JOHNSON and JOSEPH A. AMBLER (*J. Amer. Chem. Soc.*, 1911, 33, 978—985).—It has been shown by Johnson (Abstr., 1910, i, 69) that ethyl α-cyano-β-ethoxyacrylate reacts with ethyl-ψ-thiocarbamide in two ways, yielding a mixture of 5-cyano-2-ethylthiol-6-pyrimidone and ethyl 6-amino-2-ethylthiolpyrimidine-5-carboxylate.

A study has now been made of the behaviour of ethyl cyanoethoxyacrylate towards thiocarbamide, and it has been found that condensation takes place with formation of only one compound, namely, *ethyl 6-amino-2-thiopyrimidine-5-carboxylate*, $N\langle{}^{CS\text{——————}NH}_{C(NH_2)\cdot C(CO_2Et)}\rangle CH$, which crystallises in needles and decomposes at 260—265°; the *hydrochloride* decomposes at 209—211°. On hydrolysing this ester with potassium hydroxide, the corresponding *acid* (2-*thiocytosine-5-carboxylic acid*) is produced, which forms colourless prisms containing $1H_2O$, and decomposes at 253—263°. If this acid is boiled for twenty hours with 20% sulphuric acid, it is converted into 2-*thio-6-pyrimidone-5-carboxylic acid*, $NH\langle{}^{CS\text{———}NH}_{CO\cdot C(CO_2H)}\rangle CH$, m. p. 246—247° (decomp.), which forms granular crystals. An attempt which was made to desulphurise ethyl 6-amino-2-thiopyrimidine-5-carboxylate by means of chloroacetic acid resulted in the formation of 6-*amino-5-carbethoxypyrimidine-2-thioglycollic acid*, $N\langle{}^{C(S\cdot CH_2\cdot CO_2H)\cdot NH}_{C(NH_2)\text{——}C(CO_2Et)}\rangle CH$, m. p. 174—177° (decomp.), which forms a light brown powder.

When 2 : 6-dioxypyrimidine-5-acetamide, obtained by heating ethyl 2 : 6-dioxypyrimidine-5-acetate with ammonia, is treated with bromine in presence of potassium hydroxide, 4 : 5-*dibromo*-2 : 6-*dioxyhexahydropyrimidine-5-acetamide*, $NH\langle{}^{CO\text{————————}NH}_{CO\cdot CBr(CH_2\cdot CO\cdot NH_2)}\rangle CHBr$, is produced as a light yellow powder; its *picrate* crystallises in yellow needles, and decomposes above 280°. When this compound is warmed

gently with alkali hydroxide, it is transformed into 4 : 5-*dihydroxy-2 : 6-diketohexahydropyrimidine-5-acetamide*,

$$NH<\begin{matrix}CO\text{———————————}NH \\ CO\cdot C(OH)(CH_2\cdot CO\cdot NH_2)\end{matrix}>CH\cdot OH,$$

which forms minute, lemon-yellow prisms, and decomposes at about 270—280°; on reduction with hydriodic acid, it yields 2 : 6-dioxypyrimidine-5-acetic acid and ammonium iodide. 2 : 6-Dioxypyrimidine is not reduced at the double bond by hydriodic acid, but can be recovered unchanged after three hours' digestion. E. G.

Hydroxyindazoles. PAUL FREUNDLER (*Compt. rend.*, 1911, **152**, 1256—1259; *Bull. Soc. chim.*, 1911, [iv], **9**, 601—605. Compare Abstr., 1903, i, 371; 1904, i, 121, 667, 699; 1906, i, 544).—The position of the chlorine atoms in the 2 : 5-dichloro-3-hydroxy-2-phenylindazole, previously described (Abstr., 1907, i, 158), has been established by oxidising it with chromic acid, when it yields *benzeneazo*-3 : 5-*dichlorobenzoic acid*, red prisms, m. p. 142—143°; sodium hyposulphite converts this into the corresponding diamine. A mixture of phosphorus oxychloride and pentachloride converts the indazole into 2 : 5 : 7-*trichloro-3-hydroxy-2-phenylindazole*, $C_{13}H_7N_2Cl_3$, needles, m. p. 172·5°.

In their general behaviour, hydroxyindazoles resemble phenols, but have feebly basic properties. The foregoing dichloro-compound forms a *potassium* salt, a *methyl ether*, m. p. 144·5°, a *benzoyl* derivative, m. p. 204°, and an *acetyl* derivative occurring in large prisms, m. p. 133°. The *hydrochloride* is hydrolysed by water. Phosphoryl chloride forms a *compound*, $C_{13}H_8ON_2Cl,POCl_3$. Sodium hypochlorite in alkaline solution oxidises it to the corresponding azo-acid, but with the formation of an intermediate compound crystallising in green leaflets.
W. O. W.

A Negative Case of Indigotin Condensation. ELIE E. PISOVSCHI (*Bull. Soc. chim.*, 1911, [iv], **9**, 548—549).—It was to be expected that 6-nitroveratraldehyde (Pschorr and Sumuleanu, Abstr., 1900, i, 178) would give Baeyer and Drewsen's reaction, condensing with acetone in presence of an alkali to form 5 : 6 : 5′ : 6′-tetramethoxyindigotin, but whilst 2-nitroveratraldehyde in this reaction furnishes the corresponding tetramethoxyindigotin, already described by Hayduck (Abstr., 1903, i, 826), the 6-nitroveratraldehyde is recovered unchanged. T. A. H.

Constitution of Indirubin. ANDRÉ WAHL and P. BAGARD (*Bull. Soc. chim.*, 1911, [iv], **9**, 546—548).—A reply to Maillard (this vol., i, 326). T. A. H.

Constitution of Auramine. LEOPOLD SEMPER (*Annalen*, 1911, **381**, 234—264).—An attempt is made to decide between the two formulæ $C(C_6H_4\cdot NMe_2)_2\colon NH_2Cl$ and

$$NMe_2\cdot C_6H_4\cdot C(NH_2)\colon C_6H_4\colon NMe_2Cl$$

for auramine (compare Graebe, Abstr., 1899, i, 702).

Auramine differs from other dyes with a quinonoid structure in its

yellow colour and its general absorption in the blue and violet end of the spectrum, whereas most quinonoid dyes give characteristic absorption bands. A number of acylated auramine bases have been examined, more especially the acetyl derivative, and it is shown that although the bases themselves are pale yellow in colour, they yield deep bluish-violet or bluish-green compounds with acids, metallic haloids, and alkyl haloids. These compounds resemble the quinonoid diphenylmethane dyes in the following properties: (1) deep colour, (2) selective absorption, (3) instability, and (4) ability to form pale orange-yellow acid salts. The conversion of the bases by acids in either the presence or absence of water into the quinonoid salts is so marked and rapid that they can be used as indicators. These deeply coloured salts derived from acylauramines are so essentially different from the salts of auramine, of methyl- or phenyl-auramine, and of mono-, di- and tri-nitroauramines, that the conclusion is drawn that the latter group of salts cannot have a quinonoid structure, and hence Graebe's imino-structure is accepted.

The gradual change in electrical conductivity observed by Hantzsch and Osswald (Abstr., 1900, i, 256) when an equivalent quantity of alkali is added to a solution of an auramine salt is attributed to the formation of supersaturated solutions and the gradual separation of the excess of solute, and not to the slow conversion of an ammonium base into a carbonium pseudo-base. This conclusion is supported by the fact that the initial conductivity at 25° is greater than at 0°, whereas if the change in conductivity is due to molecular rearrangement, the velocity of the latter should be diminished by fall of temperature, and hence the initial conductivity increased. It is suggested that there is an equilibrium between the imonium base or its ions and the imine:

$$\colon C\colon NH_2\cdot OH \rightleftarrows \colon C\colon NH_2^{\cdot} + OH' \rightleftarrows \colon C\colon NH + H_2O,$$

and as the sparingly soluble imine separates, the equilibrium is shifted towards the right. This is supported by the fact that after the crystallisation of the imine is complete, the solution is still yellow, owing to the presence of a small amount of the $\colon C\colon NH_2^{\cdot}$ ion and the colour remains, but can be destroyed by the addition of an appreciable excess of alkali (excess of OH' ions) and restored again by the addition of much water. It is shown that the auramine base is more soluble in dilute sodium chloride solution than in water; when a colourless benzene solution of the imine is shaken with water, the aqueous solution assumes a pale colour, but when sodium chloride solution is used the aqueous layer becomes golden-yellow in colour (compare also Baeyer and Villiger, *Ber.*, 1904, 37, 2852).

Auramine is a strong base, as shown by the fact that it reacts readily with carbon dioxide; the aqueous solution of its carbonate is strongly alkaline, and its trinitro-derivative can form stable salts. This is probably due to the influence of the $\cdot NMe_2$-group on the imino-radicle.

The halochromism of amines (Kauffmann) is more pronounced when the molecule contains a number of unsaturated groups. This can be effected by introduction of olefine linkings, phenyl groups, or auxochromes. The more strongly unsaturated the molecule the deeper is

the colour tone produced by salt formation. The formation of dyes from auramine and Homolka's base by salt formation are examples of halochromism. Further examples are met with in the salts of Michler's ketone, although the salts themselves are too unstable for isolation (compare Staudinger, Abstr., 1909, i, 907; Straus and Bormann, 1910, i, 281). The additive *compound*,

$$CO(C_6H_4\cdot NMe_2)_2,SnCl_4,$$

forms a blood-red precipitate, which turns orange in contact with atmospheric moisture.

A perfectly colourless auramine base, free from carbonate and decomposition products, can be obtained by treating the pure hydrochloride with excess of dilute sodium hydroxide solution and benzene in the cold. The solution is filtered in an atmosphere of hydrogen or nitrogen, and evaporated under reduced pressure, when the base is obtained as a colourless, glistening, crystalline mass. It is not affected by light, and its benzene turns yellow on the addition of a little alcohol. An aqueous-alcoholic solution colours phenolphthalein orange-red. The *perchlorate* forms yellow crystals sparingly soluble in water. Ethereal solutions of mercuric chloride or stannic chloride yield yellow precipitates with a benzene solution of the base. The aqueous solution of the hydrochloride does not give an immediate precipitate with silver nitrate, but a precipitate is formed on warming, or on the addition of nitric acid.

Aqueous and alcoholic solutions of auramine salts have a much deeper colour when warm than when cold; magenta and acidified solutions of Michler's ketone behave similarly. An orange-coloured acid hydrochloride has been isolated by the action of excess of hydrogen chloride on the base and drying under reduced pressure. The salt is readily decomposed by the addition of most solvents.

Acetylauramine, $NAc\colon C(C_6H_4\cdot NMe_2)_2$, prepared by the action of acetic anhydride on a benzene solution of the base, crystallises from alcohol in slender, pale yellow needles, m. p. 221°, and turns blue in contact with acids, even with atmospheric carbon dioxide. Its solution in phenol has a moss-green colour, which is removed by the addition of ether.

The quinonoid *hydrochloride*, $NMe_2\cdot C_6H_4\cdot C(NHAc)\colon C_6H_4\colon NMe_2Cl$, crystallises in glistening, green needles, containing 1EtOH. Its aqueous solution has a violet-blue colour or in deep layers, a red colour. The salt reacts readily with warm water or acids, yielding Michler's ketone and acetamide, but the primary product in the case of acids is a diacid salt, which has an orange colour and is stable in the presence of excess of acid. With mercuric chloride, acetylauramine yields an additive *compound* in the form of deep coloured crystals. The *methiodide*, $NMe_2\cdot C_6H_4\cdot C(NMeAc)\colon C_6H_4\colon NMe_2I$, forms a hygroscopic solid, which readily loses methyl iodide; its aqueous and alcoholic solutions have a greenish-blue colour, and its absorption spectrum resembles that of the hydrochloride. With picryl chloride, acetylauramine forms a reddish-violet additive *compound*, which is readily dissociated. As an indicator, it approaches phenolphthalein, and gives a reaction with a hydrion concentration of 10^{-8}. It has the drawback that it is fairly readily decomposed by water or acids, and should, therefore, be added just before the end of the titration.

Benzoylauramine (Finkh and Schwimmer, Abstr., 1895, i, 184) yields a quinonoid *chloride*, $NMe_2\cdot C_6H_4\cdot C(NHBz):C_6H_4:NMe_2Cl$, in the form of a dark violet, hygroscopic powder.

Benzenesulphonylauramine, $SO_2Ph\cdot N:C(C_6H_4\cdot NMe_2)_2$, crystallises from ethyl acetate in glistening, yellow prisms, m. p. 182°. Its solutions in phenol or glacial acetic acid have a reddish-brown colour, the hydrochloride and oxalate are unstable, and it yields a green *compound* with stannic chloride.

4-*Nitrophenylauramine*, $NO_2\cdot C_6H_4\cdot N:C(C_6H_4\cdot NMe_2)_2$, obtained by heating auramine base with *p*-nitroaniline at 160°, separates from ethyl acetate in dark yellow crystals, m. p. 226°. Its solutions in phenol and glacial acetic acid have a blood-red colour similar to the hydrochloride. 2 : 4-*Dinitrophenylauramine*, $C_{23}H_{23}O_4N_5$, obtained by condensing auramine with chloro-2 : 4-dinitrobenzene in benzene solution, crystallises from amyl alcohol as a brick-red powder. The *hydrochloride* forms a dark red, hygroscopic mass.

2 : 4 : 6-*Trinitrophenylauramine*, $C_{23}H_{22}O_6N_6,\frac{1}{2}C_6H_6$, forms large, glistening, black prisms, and loses its benzene at 150°. It crystallises from alcohol in glistening, red needles, m. p. 211°, and is only slowly decomposed by acids. The *hydrochloride*, $C_{23}H_{23}O_6N_6Cl$, forms glistening, bronzy needles. J. J. S.

Quinazolines. XXVII. Synthesis of 3-Aminoaryl-4-quinazolones from Acylanthranils and Aromatic Diamines. MARSTON T. BOGERT, ROSS A. GORTNER, and CARL G. AMEND (*J. Amer. Chem. Soc.*, 1911, 33, 949—962).—The work on the synthesis of quinazolines from acylanthranils and primary amines (this vol., i, 162, and previous abstracts) has been extended to the aromatic diamines. The condensation in this case is remarkably smooth, and can be best effected by gently fusing a mixture of the reagents. The diamine must possess one primary amino-group, whilst the other may be primary, secondary, or tertiary. The aminoarylquinazolones thus produced, which contain a primary amino-group, are crystalline or pulverulent solids, and when diazotised in the usual way yield diazo- or tetra-azo-compounds, which unite with suitable couplers to form valuable azo-dyes. The following diamines were used: *o*-, *m*-, and *p*-phenylenediamines, 2 : 4′- and 2 : 5′-tolylenediamines, benzidine, *o*-tolidine, 3-ethoxybenzidine, and di-*o*-anisidine. All these condensed smoothly to form aminoarylquinazolones, except *o*-phenylenediamine. Condensations have also been carried out with di- and poly-amines containing only one primary amino-group. The acylanthranils employed were acetylanthranil, 5-bromoacetylanthranil, 5-nitroacetylanthranil, 4- and 5-acetylaminoacetylanthranils, benzoylanthranil, and *m*- and *p*-nitrobenzoylanthranils. The benzoylanthranils do not yield aminoarylquinazolones, but diquinazolonyl compounds. In this paper, corrected m. p.'s are recorded in all cases, except where otherwise stated.

m-*Nitrobenzoylanthranilic acid*, $CO_2H\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2$, m. p. 233·5°, obtained by the action of *m*-nitrobenzoyl chloride on sodium anthranilate, forms colourless prisms. p-*Nitrobenzoylanthranilic acid*, m. p. 235·5°, prepared in a similar manner,

crystallises in nearly colourless needles. m-*Nitrobenzoylanthranil*, $C_6H_4<\begin{array}{l}CO\\ \vert\\ N\cdot CO\cdot C_6H_4\cdot NO_2\end{array}$, m. p. 167—168°, forms small, almost colourless needles, and p-*nitrobenzoylanthranil*, m. p. 207°, light yellow needles.

The following compounds were obtained by the condensation of aromatic diamines with acetylanthranil. 3-m-*Aminophenyl*-2-*methyl*-4-*quinazolone*, $C_6H_4<\begin{array}{l}N{=\!=}CMe\\ \quad\ \ \vert\\ CO-N\cdot C_6H_4\cdot NH_2\end{array}$, m. p. 210°, from *m*-phenylenediamine. In one experiment, an aqueous solution of *m*-phenylenediamine was treated with acetylanthranil, and the product recrystallised from alcohol. On diluting the mother liquor, another *substance*, m. p. 158°, separated, which contained 10·22% of nitrogen. 3-p-*Aminophenyl*-2-*methyl*-4-*quinazolone*, m. p. 220°, from *p*-phenylenediamine. In one case, this substance was found to be accompanied by a small quantity of 3 : 3′-*phenylenebis*-2-*methyl*-4-*quinazolone*,

$$C_6H_4<\begin{array}{l}N{=\!=}CMe\qquad CMe\colon N\\ \quad\ \ \vert\qquad\qquad\quad \vert\\ CO-N\cdot C_6H_4\cdot N{-\!-}CO\end{array}>C_6H_4,$$

m. p. above 300°. 3-m-*Aminotolyl*-2-*methyl*-4-*quinazolone*, m. p. 131·4°, from 2 : 4-tolylenediamine. *Acetylanthranyl*-m-*aminotoluidide*, m. p. 137—138°, forms stellate groups of colourless needles. 3-p-*Aminotolyl*-2-*methyl*-4-*quinazolone*, m. p. 169°, from 2 : 5-tolylenediamine. 3-(4′-*Aminodiphenyl*)-2-*methyl*-4-*quinazolone*,

$$C_6H_4<\begin{array}{l}N{=\!=}CMe\\ \quad\ \ \vert\\ CO-N\cdot C_6H_4\cdot C_6H_4\cdot NH_2\end{array},$$

m. p. 282—283°, from benzidine. 3-(4′-*Aminoditolyl*)-2-*methyl*-4-*quinazolone*, m. p. 80—81°, from *o*-tolidine. 3-(4′-*Aminoethoxydiphenyl*)-2-*methyl*-4-*quinazolone*, $C_6H_4<\begin{array}{l}N{=\!=}CMe\\ \quad\ \ \vert\\ CO-N\cdot C_6H_3(OEt)\cdot C_6H_4\cdot NH_2\end{array}$ or $C_6H_4<\begin{array}{l}N{=\!=}CMe\\ \quad\ \ \vert\\ CO-N\cdot C_6H_4\cdot C_6H_3(OEt)\cdot NH_2\end{array}$, m. p. 86—87°, from ethoxybenzidine. 3-(4′-*Aminodianisyl*)-2-*methyl*-4-*quinazolone*, m. p. 72—73°, from *o*-dianisidine.

The following compounds were prepared by condensation with derivatives of acetylanthranil. 6-*Bromo*-3-p-*aminodiphenyl*-2-*methyl*-4-*quinazolone*, $C_6H_3Br<\begin{array}{l}N{=\!=}CMe\\ \quad\ \ \vert\\ CO-N\cdot C_6H_4\cdot C_6H_4\cdot NH_2\end{array}$, m. p. 198—199°, from 5-bromoacetylanthranil and benzidine. 6-*Nitro*-3-p-*aminophenyl*-2-*methyl*-4-*quinazolone*, m. p. 259—260° (decomp.), from 5-nitroacetylanthranil and *p*-phenylenediamine. 6-*Acetylamino*-3-p-*aminophenyl*-2-*methyl*-4-*quinazolone*, m. p. 280° (uncorr.), from 3-acetylaminoacetylanthranil and *p*-phenylenediamine. 7-*Acetylamino*-3-m-*aminophenyl*-2-*methyl*-4-*quinazolone*, m. p. above 310°, from 4-acetylaminoacetylanthranil and *m*-phenylenediamine. 7-*Acetylamino*-3-p-*aminophenyl*-2-*methyl*-4-*quinazolone*, m. p. above 360°; when this substance is boiled with 20% hydrochloric acid, a purple solution is obtained, which, on treatment with sodium hydroxide, yields 7-*amino*-3-p-*aminophenyl*-2-*methyl*-4-*quinazolone*, m. p. 287°. 7-*Acetylamino*-3-*aminotolyl*-2-*methyl*-4-*quinazolone*, m. p. 290°, from 4-acetylaminoacetylanthranil and

2·4-tolylenediamine, yields an *acetyl* derivative, m. p. 268·5°, and when boiled with 10% hydrochloric acid gives 7-*amino*-3-*aminotolyl*-2-*methyl*-4-*quinazolone*, m. p. 262°. 7-*Acetylamino*-3-(4′-*aminodiphenyl*)-2-*methyl*-4-*quinazolone*, $NHAc\cdot C_6H_3 < \begin{matrix} N{=}CMe \\ CO{-}N\cdot C_6H_4\cdot C_6H_4\cdot NH_2 \end{matrix}$, m. p. 296—297°, from 4-acetylaminoacetylanthranil and benzidine; this compound is accompanied by another *substance*, m. p. 256° (decomp.), which is probably the corresponding diquinazolonyl compound. 7-*Acetylamino*-3-(4′-*aminoditolyl*)-2-*methyl*-4-*quinazolone*, m. p. 120—125° (decomp.), from 4-acetylaminoacetylanthranil and *o*-tolidine. 7-*Acetylamino*-3-(4′-*amino*-?-*ethoxydiphenyl*)-2-*methyl*-4-*quinazolone*, m. p. about 105—110°, from 4-acetylaminoacetylanthranil and ethoxybenzidine. 7-*Acetylamino*-3-(4′-*aminodianisyl*)-2-*methyl*-4-*quinazolone*, m. p. about 144°, from 4-acetylaminoacetylanthranil and di-*o*-anisidine, yields a *tetra-acetyl* derivative, m. p. 239°.

Anschütz, Schmidt, and Greiffenberg (Abstr., 1903, i, 58) have shown that when ammonia is passed into a boiling alcoholic solution of benzoylanthranil, *o*-benzoylaminobenzamide is produced. It is now found that if benzoylanthranil is boiled with excess of a strong aqueous solution of ammonia, a compound, probably *di*-o-*benzoylaminodibenzamide*, $(NHBz\cdot C_6H_4\cdot CO)_2NH$, m. p. 118°, is formed, which, when boiled with potassium hydroxide solution, is converted into 2-phenyl-4-quinazolone. When benzoylanthranil is heated with *p*-phenetidine, a *compound*, m. p. 213°, is produced. 3 : 3′-m-*Phenylenebis*-2-m-*nitrophenyl*-4-*quinazolone*,

$$C_6H_4 < \begin{matrix} N{=}C\cdot C_6H_4\cdot NO_2 \\ CO\cdot N{-}{-}{-}{-} \end{matrix} C_6H_4 \begin{matrix} NO_2\cdot C_6H_4\cdot C{=}N \\ {-}{-}{-}{-}N\cdot CO \end{matrix} > C_6H_4,$$

m. p. 226°, is obtained by the action of *m*-nitrobenzoylanthranil on *m*-phenylenediamine. The corresponding *p*-nitrophenyl derivative, m. p. 207°, is produced when *p*-nitrobenzoylanthranil is used.

E. G.

Hydrazones of Phenacylamines. MAX BUSCH and GEORG HEFELE (*J. pr. Chem.*, 1911, [ii], 83, 425—453).—With the hope of obtaining a direct proof of the stereoisomerism of hydrazones, the evidence for which at present is based chiefly on analogy with the stereoisomerism of the oximes, the authors have prepared hydrazones of amino-ketones of the type $Ar\cdot CO\cdot CH_2\cdot NHR$, the *syn*-forms of which, by intramolecular reaction of the hydrazino- and the amino- (or substituted amino-) groups, might be expected to undergo ring closure. Many amino-ketones of the preceding type have been prepared, but only in the case of the ψ-cumidine derivative,

$$COPh\cdot CH_2\cdot NH\cdot C_9H_{11},$$

have two forms of the phenylhydrazone been isolated; unfortunately, one form has been obtained in amount so small that the special purpose of the research has not been fulfilled. The phenylhydrazones condense with aldehydes to form tetrahydrotriazines, and are readily oxidised by an excess of the hydrazine or by chromic acid to dihydro-1 : 2 : 3-triazoles, which are reduced by sodium and alcohol to tetrahydrotriazoles.

The authors' goal has not been reached by an examination of the semicarbazones and thiosemicarbazones of the preceding amino-ketones; the semicarbazones show a tendency to yield ketotetrahydrotriazines. Only with amino-ketones of the type $COPh\cdot CH_2\cdot NR_2$ have two forms of the phenylhydrazone been obtained; in these cases, unfortunately, the configurations cannot be determined by the authors' method, because ring closure cannot occur. Phenacylamines, $COPh\cdot CH_2\cdot NHR$, are readily obtained by the interaction of ω-bromoacetophenone and an amine (2 mols.) in alcoholic solution. The hydrazones are obtained in about 80% yield by adding a small excess of the hydrazine to a suspension of the amino-ketone in cold alcohol containing a little acetic acid and also hydrogen sulphide to prevent the oxidation of the hydrazone to the dihydrotriazole.

The following new compounds have been prepared by the preceding methods.

ω-Benzylaminoacetophenone forms a *phenylhydrazone*,

$$NHPh\cdot N\colon CPh\cdot CH_2\cdot NH\cdot CH_2Ph,$$

m. p. 76°, an alcoholic solution of which is converted by boiling glacial acetic acid into a *substance*, m. p. 176°, which is probably the dihydrotriazole. With phenylhydrazine, ω-anilinoacetophenone yields 1 : 2 : 4-*triphenyl*-2 : 5-*dihydro*-1 : 2 : 3-*triazole*, $NPh<\begin{matrix}N{=}CPh\\ NPh\cdot CH_2\end{matrix}$, m. p. 136·5°, whilst with semicarbazide and thiosemicarbazide it yields the *semicarbazone*, m. p. 171° (decomp.), and *thiosemicarbazone*, m. p. 167° (decomp.), respectively; the former forms a *hydrochloride*, m. p. 230° (decomp.), and at 200° loses ammonia, yielding 2-*keto*-1 : 5-*diphenyl*-1 : 2 : 3 : 6-*tetrahydro*-1 : 3 : 4-*triazine*, $NPh<\begin{matrix}CO{-}NH\\ CH_2\cdot CPh\end{matrix}>N$, m. p. 181° (decomp.). ω-*p*-Toluidinoacetophenone forms a *phenylhydrazone*, $C_{21}H_{21}N_3$, m. p. 147°, which reacts with phenylcarbimide on the water-bath to form a *carbamide*,

$$NHPh\cdot CO\cdot NPh\cdot N\colon CPh\cdot CH_2\cdot NH\cdot C_6H_4Me,$$

m. p. 184°, and with benzoyl chloride in pyridine, yielding a *benzoyl* derivative, $NPhBz\cdot N\colon CPh\cdot CH_2\cdot NH\cdot C_6H_4Me$, m. p. 110°. The preceding phenylhydrazone reacts with benzaldehyde at 120° and with salicylaldehyde at 150° to form *substances* (which are probably tetrahydrotriazines), which have various m. p.'s (decomp.) on account of their property of retaining variable quantities of different solvents. The phenylhydrazone is also readily converted into 2 : 4-*diphenyl*-1-p-*tolyl*-2 : 5-*dihydro*-1 : 2 : 3-*triazole*, $C_6H_4Me\cdot N<\begin{matrix}CH_2\cdot CPh\\ NPh\cdot N\end{matrix}$, m. p. 152°, which does not react with phenylcarbimide, aldehydes, nitrous acid, or benzoyl chloride, and is reduced by sodium and alcohol to the *tetrahydrotriazole*, $C_{21}H_{21}N_3$, m. p. 122°. ω-*p*-Toluidinoacetophenone forms a *semicarbazone*, $C_{16}H_{18}ON_4$, m. p. 182° (decomp.), which evolves ammonia at 205°, and yields the 2-*keto*-5-*phenyl*-1-p-*tolyldihydro*-1 : 3 : 4-*triazine*, $C_6H_4Me\cdot N<\begin{matrix}CO{-}NH\\ CH_2\cdot CPh\end{matrix}>N$, m. p. 208°. ω-o-*Anisidinoacetophenone*, $OMe\cdot C_6H_4\cdot NH\cdot CH_2\cdot COPh$, yellow needles, m. p. 89°, forms a *semicarbazone*, $C_{16}H_{18}O_2N_4$, m. p. 176° (decomp.), and a

phenylhydrazone, $C_{21}H_{21}ON_3$, m. p. 105°; from the latter is obtained the 2 : 4-*diphenyl*-1-o-*anisyldihydro*-1 : 2 : 3-*triazole*,

$$OMe\cdot C_6H_4\cdot N<\begin{matrix}CH_2-CPh,\\ NPh\cdot N\end{matrix}$$

m. p. 151·5°. The reaction between ω-bromoacetophenone and *p*-anisidine yields three products: ω-p-*anisidinoacetophenone*, m. p. 93°, yellow leaflets (which differs from all the other phenacylamines by giving a violet coloration with alcoholic ferric chloride), a *substance*, m. p. 181°, crystallising in orange-yellow plates, and *diphenacyl*-p-*anisidine*, $OMe\cdot C_6H_4\cdot N(CH_2\cdot COPh)_2$, m. p. 180°, yellow needles. ω-*p*-Anisidinoacetophenone forms a *semicarbazone*, m. p. 145° (decomp.), and an oily phenylhydrazone, from which the corresponding *dihydrotriazole*, $C_{21}H_{19}ON_3$, m. p. 156°, is obtained; ω-*p*-chloroanilinoacetophenone forms a *semicarbazone*, $C_{15}H_{17}ON_4Cl$, m. p. 167° (decomp.), and a *phenylhydrazone*, m. p. 147°, from which 2 : 4-*diphenyl*-1-p-*chlorophenyldihydro*-1 : 2 : 3-*triazole*, $C_{20}H_{16}N_3Cl$, m. p. 153°, is obtained.

ω-ψ-*Cumidinoacetophenone*, $C_6H_2Me_3\cdot NH\cdot CH_2\cdot COPh$, yellow needles, m. p. 122°, forms a *semicarbazone*, m. p. 179° (decomp.), and a *phenylhydrazone*, m. p. 155°; from the mother liquor in the latter preparation a very small amount of a yellow *substance*, m. p. 118°, is sometimes obtained, which crystallises in rhombohedra, and shows the reactions of a hydrazone. From the phenylhydrazone, m. p. 155°, is obtained 2 : 4-*diphenyl*-1-ψ-*cumyldihydro*-1 : 2 : 3-*triazole*, $C_{23}H_{23}N_3$, m. p. 139°.

ω-Dibenzylaminoacetophenone yields two isomeric *phenylhydrazones*, which are separated by alcohol; the less soluble form crystallises in colourless leaflets, m. p. 107°, the more soluble in needles, m. p. 75°. The latter change to the former at 105°, or by treating an alcoholic solution of the needles with hydrogen chloride and basifying the resulting *hydrochloride*, m. p. 255° (decomp.), with ammonia.

ω-Phenylmethylaminoacetophenone forms a *phenylhydrazone*, $C_{21}H_{21}N_3$, m. p. 98°, and a *semicarbazone*, $C_{16}H_{18}ON_4$, m. p. 202° (decomp.). ω-Phenylethylaminoacetophenone forms, in the absence of air, two isomeric *semicarbazones*, $C_{17}H_{20}ON_4$, one, m. p. 153°, crystallising in leaflets, the other, m. p. 145°, in needles. C. S.

[Preparation of a Carbamide Derivative.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 231448).—2 : 2′-*Diamino*-4 : 4′-*dihydroxy*-s-*diphenylcarbamide*-6-6′-*disulphonic acid*,

$$CO[NH\cdot C_6H_2(NH_2)(OH)\cdot SO_3H]_2,$$

prepared by the action of carbonyl chloride on 2-nitro-4 : 1-aminophenol-6-sulphonic acid with subsequent reduction is of value in the preparation of azo-dyes. F. M G. M.

Xanthine Substances from Uric Acid. ERNST EDW. SUNDWIK (*Skand. Arch. Physiol.*, 1911, 25, 256—258. Compare Abstr., 1899, i, 174).—The author finds that calcium urate when heated yields xanthine. A mixture of equal weights of uric acid, calcium formate, and calcium hydroxide is moistened with water until it sets (formation of calcium urate), and the roughly powdered mass is then gradually

heated in a tube in a combustion furnace until evolution of gas begins. The xanthine is precipitated by acidifying the solution of the product, the uric acid removed as acid ammonium urate, and the xanthine finally obtained in the form of its silver nitrate compound.

R. V. S.

Hydroxyazo-compounds and Ketohydrazones. IV—VI. KARL AUWERS (*Annalen*, 1911, **381**, 265—312. Compare Abstr., 1908, i, 477; this vol., i, 168).—The three diketones, 4-methylcoumarandione, thionaphthenquinone, and isatin, yield α- and β-monophenylhydrazones, and an investigation of these derivatives by the methods already described shows that they possess the hydrazone and not the azo-structure.

IV. Phenylhydrazone Derivatives of 4-Methylcoumarandione. [With R. APITZ.]—The 2-*phenylhydrazone* of 4-methylcoumarandione (Fries, Abstr., 1909, i, 175), $C_6H_3Me<{C(N_2HPh) \atop O}>CO$, crystallises from dilute acetic acid in light yellow needles, m. p. 148°, and dissolves in concentrated sulphuric acid to a brownish-red solution. When left in contact with aqueous-alcoholic sodium hydroxide solution for fifteen to thirty minutes and then acidified, it yields the *phenylhydrazone* of 4-hydroxy-*m*-tolylglyoxylic acid (Fries and Finck, Abstr., 1909, i, 43), which crystallises from dilute alcohol in greenish-yellow needles, m. p. 160° (decomp.). The same product can be obtained by the action of phenylhydrazine on the ketonic acid, and when heated for five minutes with glacial acetic acid the lactone is re-formed. 4-*Methylcoumarandione*-2-*benzoylphenylhydrazone*,

$$C_6H_3Me<{C(N\cdot NPhBz) \atop O}>CO,$$

prepared by the action of an aqueous solution of benzoylphenylhydrazine hydrochloride on a methyl-alcoholic solution of the ketone, forms colourless needles, m. p. 168—169°, and yields an orange-yellow solution in concentrated sulphuric acid, and when its solution in ethyl acetate is reduced with zinc dust and glacial acetic acid in the cold, benzanilide is formed, but not aniline. Aqueous alcoholic sodium hydroxide converts the benzoylphenylhydrazone into the *benzoylphenylhydrazone* of 4-hydroxy-*m*-tolylglyoxylic acid,

$$C_{22}H_{18}O_4N_2,$$

which forms small, colourless crystals, m. p. 112° (decomp.).

The *phenylhydrazone* of *4-hydroxy*-m-*tolylglyoxylic acid phenylhydrazide*, $OH\cdot C_6H_3Me\cdot C(N_2HPh)\cdot CO\cdot NH\cdot NHPh$, obtained by boiling an alcoholic solution of the 4-methylcoumarandione with an excess of free phenylhydrazine, crystallises in colourless needles, m. p. 183°, and reduces Fehling's solution.

4-*Methylcoumarandione*-1-*phenylhydrazone*,

$$C_6H_3Me<{CO \atop O}>C:N\cdot NHPh,$$

can be prepared by condensing the diketone with benzenediazonium chloride in alkaline or in acetic acid solution, and crystallises from boiling alcohol in golden-yellow plates, m. p. 224°. Its solution in concentrated sulphuric acid has a cherry-red colour. So far acetyl

derivatives have not been prepared. The *osazone*,

$$C_6H_3Me<\underset{O\text{—————}}{\overset{C(N_2HPh)}{}}>C\colon N_2HPh,$$

obtained by warming the 1-phenylhydrazone with excess of phenylhydrazine on the water-bath, crystallises from glacial acetic acid in golden-yellow plates, m. p. 223°, and does not reduce Fehling's solution.

V. Phenylhydrazone Derivatives of Thionaphthenquinone. [With Karl Müller.]—Thionaphthenquinone-2-phenylhydrazone (Bezdrik, Friedländer, and Koeniger, Abstr., 1908, i, 201) has m. p. 165—166°, and does not yield an osazone. With warm dilute alkalis, it yields the *phenylhydrazone* of thiolphenylglyoxylic acid,

$$SH\cdot C_6H_4\cdot C(CO_2H)\colon N\cdot NHPh,$$

m. p. 80—86°, but this is rapidly transformed into the original phenylhydrazone when warmed with various solvents. The 2-phenylhydrazone of the diketone reacts with methyl iodide and sodium methoxide in the cold, yielding the *dimethyl* derivative of the phenylhydrazone of 2-thiolphenylglyoxylic acid,

$$SMe\cdot C_6H_4\cdot C(CO_2Me)\colon N\cdot NHPh,$$

which crystallises from alcohol in pale yellow, flat needles, m. p. 107·5°. When boiled with sodium hydroxide solution it yields the *monomethyl ether*, $SMe\cdot C_6H_4\cdot C(CO_2H)\colon N\cdot NHPh$, in the form of sulphur-yellow needles, m. p. 180° (decomp.).

Thionaphthenquinone-2-benzoylphenylhydrazone,

$$C_6H_4<\underset{S\text{—————}}{\overset{C(N\cdot NPhBz)}{}}>CO,$$

prepared by condensing the ketone with benzoylphenylhydrazine hydrochloride in hot alcoholic solution, crystallises in brilliant, deep red, flat needles, m. p. 199°. It is readily hydrolysed to the corresponding phenylhydrazone, and when its solution in ethyl acetate is reduced with zinc dust and glacial acetic acid in the cold, no trace of aniline is obtained. *Thionaphthenquinone-2-phenylmethylhydrazone*, $C_{15}H_{12}ON_2S$, crystallises from alcohol in dark red, glistening needles, m. p. 98—99°. When heated with excess of phenylmethylhydrazine for four hours at 130°, an *isomeride* is obtained, which crystallises in sulphur-yellow prisms, m. p. 122—123°.

Thionaphthenquinone-1-phenylhydrazone, $C_6H_4<\underset{S}{\overset{CO}{}}>C\colon N\cdot NHPh$, crystallises in flat, glistening, reddish-brown prisms, has m. p. 194°, and is identical with Friedländer's 1-benzeneazo-2-hydroxythionaphthen (Abstr., 1909, i, 504). It is also formed by condensing phenylhydrazine with the ketodibromide, and with excess of phenylhydrazine at 100° yields the *osazone*, $C_6H_4<\underset{S\text{———}}{\overset{C(N_2HPh}{}}>C\colon N_2HPh$, which crystallises from benzene in slender, orange-yellow needles, m. p. 199—200°. The 1-phenylhydrazone reacts with benzoyl chloride in the presence of 9% sodium hydroxide solution, yielding the *1-benzoylphenylhydrazone*, $C_6H_4<\underset{S}{\overset{CO}{}}>C\colon N\cdot NPhBz$, which exists in two modifications, the one crystallises from glacial acetic acid and a little water in yellow needles or orange-yellow prisms, and has m. p. 156°

the other crystallises from alcohol in ruby-red rhombs or carmin-red, pointed prisms with a blue shimmer. Both compounds when reduced with zinc dust and glacial acetic acid yield benzanilide, but no trace of aniline.

When the 1-phenylhydrazone is methylated by means of methyl sulphate in the presence of sodium hydroxide or of methyl iodide and sodium methoxide, a mixture of *O*- and *N*-methyl derivatives is obtained. *Thionaphthenquinone-1-phenylmethylhydrazone*, $C_{15}H_{12}ON_2S$, is sparingly soluble in ether, crystallises from alcohol in long, lustrous, red needles, m. p. 133—134°, and on reduction yields methylaniline. It is also formed when 2-dibromo-3-ketodihydrothionaphthen is condensed with phenylmethylhydrazine. *1-Benzeneazo-2-methoxythionaphthen*, $C_6H_4<\substack{C(OMe)\\O}>C\cdot N{:}NPh$, is readily soluble in ether, and crystallises in orange-yellow plates, or from glacial acetic acid in carmine-red, pointed needles. Its solutions are mostly golden-yellow coloured, whereas those of the isomeric *N*-methyl derivative have an orange-red colour. When reduced the *O*-ether yields aniline.

The *benzoyl* derivative of 1-thionaphthenquinoneoxime,

$$C_6H_4<\substack{CO\\S}>C{:}N\cdot OBz,$$

obtained by benzoylating the oxime in the presence of pyridine, crystallises from benzene in glistening, sulphur-yellow prisms, m. p. 170°, and on hydrolysis yields *o*-thiolbenzoic acid. When warmed with phenylhydrazine and glacial acetic acid the benzoyl derivative yields thionaphthenquinone-1-phenylhydrazone. The 2-phenylhydrazone of thionaphthenquinone-1-oxime (D.R.-P. 213458) crystallises from alcohol in glistening, golden-yellow, felted needles, m. p. 172° (not 154°, compare D.R.-P. 213458), and when boiled for five minutes with excess of phenylhydrazine yields the osazone. The O-*acetate*,

$$C_6H_4<\substack{C(N_2Ph)\\S}>C{:}NOAc,$$

crystallises from benzene in compact, golden-yellow prisms, m. p. 156—157°. The corresponding O-*benzoyl* derivative forms golden-yellow, felted needles, m. p. 141—142°.

Thionaphthenphenylosotriazole, $\begin{array}{l}C_6H_4\cdot C{:}N\\ \vert\qquad\quad \vert\\ S\text{——}C{:}N\end{array}>NPh$, obtained by the action of sodium hydroxide solution on an alcoholic solution of the *O*-acetyl or *O*-benzoyl derivative, forms colourless, glistening needles, m. p. 152°, and is extremely stable.

[With F. Arndt.]—4-*Methylthionaphthenquinone-1-phenylhydrazone*, $C_6H_3Me<\substack{CO\\S}>C{:}N_2HPh$, prepared from hydroxy-4-methylthionaphthen (Auwers and Arndt, Abstr., 1909, i, 175) and benzenediazonium chloride in the presence of alkali, crystallises in dark brick-red needles with a strong greenish-yellow shimmer and has m. p. 186·5°.

The *benzoyl* derivative, $C_{22}H_{16}O_2N_2S$, exists in two forms, the one crystallises from alcohol in glistening, orange-yellow needles, m. p. 145°, and the other from benzene and light petroleum in sulphur-yellow prisms, m. p. 157°. By benzoylating in the presence of

pyridine the more readily fusible compound is the chief product. The corresponding 1-*oxime*, $C_6H_3Me<\substack{CO \\ S}>C:N\cdot OH$, crystallises in glistening, yellow plates and flat needles, m. p. 188° (decomp., when fairly quickly heated). The *dibenzoyl* derivative of 4-methyl-2-hydroxy-1-aminothionaphthen, $C_6H_3Me<\substack{C(OBz) \\ S}\geqslant C\cdot NHBz$, obtained by reducing the oxime and benzoylating the product, crystallises from benzene in colourless plates, m. p. 233·5°.

VI. Isatinphenylhydrazones.—[With A. BOENNECKE.]—*Isatin 3-benzoylphenylhydrazone*, $C_6H_4<\substack{C(N\cdot NPhBz) \\ NH}>CO$ or

$$C_6H_4<\substack{C(N\cdot NPhBz) \\ N}\geqslant C\cdot OH,$$

obtained by condensing an alkaline solution of isatin with benzoylphenylhydrazine hydrochloride, crystallises from benzene in slender orange-coloured needles, m. p. 195—196°, and with alcoholic sodium hydroxide solution yields the phenylhydrazone and benzoic acid ; when reduced with zinc dust and glacial acetic acid, no trace of aniline is obtained.

1-*Benzoylisatin-3-phenylhydrazone*, $C_6H_4<\substack{C(N_2HPh) \\ NBz}>CO$, obtained by benzoylating isatin-3-phenylhydrazone by the Schotten-Baumann method or in the presence of pyridine, crystallises in golden-yellow, felted needles, m. p. 203°, and on reduction with zinc dust and glacial acetic acid yields large quantities of aniline, but no benzanilide. The same benzoyl derivative is formed when *N*-benzoylisatin is condensed with phenylhydrazine.

Isatin-β-acetylphenylhydrazone, $C_{16}H_{13}O_2N_3$, prepared from isatin and acetylphenylhydrazine, forms small, pale yellow, octahedral crystals, m. p. 199°, and is readily hydrolysed to the 3-phenylhydrazone of isatin (Fischer, Abstr., 1884, 1151). The 1-acetyl-3-phenylhydrazone (Schunck and Marchlewski, Abstr., 1895, i, 288) has m. p. 132—134°, and on reduction yields aniline, but no acetanilide, and is therefore the *N*- and not the *O*-acetyl derivative.

Isatin-2-phenylhydrazone (Heller, Abstr., 1907, i, 442) yields an N-*benzoyl* derivative, $C_6H_4<\substack{CO \\ NBz}>C:N_2HPh$, which crystallises in slender, yellow, felted needles, m. p. 188—189°. It is not hydrolysed by cold alcoholic potassium hydroxide, but when warmed yields the 2-phenylhydrazone, and when reduced yields aniline. J. J. S.

The Diacetyl Reaction for Proteins. ARTHUR HARDEN and DOROTHY NORRIS (*J. Physiol.*, 1911, **42**, 332—336).—Acetylmethylcarbinol, a product of growth of certain bacteria on sugars, is readily oxidised to diacetyl (dimethyl diketone), which then combines in the presence of alkali with some part of the protein molecule, imparting to the solution a pink colour and green fluorescence. It is now shown that the group in protein on which the reaction depends is $NH:C(NH_2)\cdot NH\cdot R$, but the exact significance of R has not yet been worked out. Only complex protein substances give any fluorescence,

and this is lost if time is allowed for hydrolysis to occur before the dimethyl diketone is added. W. D. H.

Cleavage Products Obtained by the Partial Hydrolysis of Proteins. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1911, 72, 1—14).—The fibroin of Canton and Bengal silks was subjected to hydrolysis with 70% sulphuric acid at 25° for four days. It was found that *d*-alanyl-glycine which was obtained in previous experiments on fibroin had been split into its components, but the tripeptide *d*-alanyl-glycyl-*l*-tyrosine, identical with Fischer's synthetic product, was separated out. This is the first instance of a tripeptide actually obtained by protein hydrolysis. From the horny material of the cow's hoof, a polypeptide was similarly obtained, which yielded on further hydrolysis tyrosine, cystine, tryptophan, glutamic acid, and other amino-acids. Another polypeptide, not fully identified, was obtained by the action of trypsin on casein. W. D. H.

The Refractive Indices of Solutions of Certain Proteins. V. Gliadin. T. BRAILSFORD ROBERTSON and J. E. GREAVES (*J. Biol. Chem.*, 1911, 9, 181—184).—The value of a in the equation $n - n_1 = ac$, where n is the refractive index of the solution of the protein, n_1 that of the solvent, and c the percentage concentration of the protein, was determined for gliadin in various solvents. In the less highly refractive solvents, the introduction of gliadin increases the refractive index, but in the most highly refractive solvent employed, namely, 75% phenol, the addition of gliadin reduces the refractive index. W. D. H.

Hydrolysis of Casein. THOMAS B. OSBORNE and H. H. GUEST (*J. Biol. Chem.*, 1911, 9, 333—353).—The methods of preparing the casein and estimating its hydrolytic products are given with full details. A table is finally drawn up from the results of the authors and of others of the cleavage products; 36·4% of the nitrogen is still left unaccounted for. The calculations give no evidence that casein differs in constitution to any marked degree from other proteins that do not contain phosphorus. W. D. H.

The Composition of Certain Substances Produced by the Action of Pepsin on the Products of the Complete Peptic Hydrolysis of Casein. T. BRAILSFORD ROBERTSON and H. C. BIDDLE (*J. Biol. Chem.*, 1911, 9, 295—302).—The term para-nuclein is adopted for the precipitate obtained when pepsin acts on neutral or faintly acid solutions of caseinates. When this is subjected to partial digestion by weak alkalis, the product obtained is poorer in phosphorus, and is called paranuclein-A. The two contain the same amount of carbon, hydrogen, and nitrogen, and differ from most other proteins by their low content of carbon. The synthetic product obtained at 60—70° by the action of concentrated pepsin on unconcentrated products of complete peptic hydrolysis of casein is identical so far as carbon, hydrogen, and nitrogen are concerned with

para-nuclein. If the products of hydrolysis are concentrated, the synthetic product contains more carbon, but this is attributed to contamination. W. D. H.

Substances Accompanying Oxyhæmoglobin in its Crystallisation. Pierre Thomas (*Compt. rend.*, 1911, **152**, 1424—1426).—Solvents such as ether, light petroleum, and chloroform extract small quantities of pale coloured substances from crystallised oxyhæmoglobin, but the amount hitherto obtained is insufficient to determine their nature. Light petroleum extracts 0·03—0·04% of a crystalline material, possibly a mixture of cholesterol esters. W. O. W.

Reduction of Oxyhæmoglobin. Jules Wolff (*Compt. rend.*, 1911, **152**, 1332—1334).—Ewald (Abstr., 1907, ii, 184) has stated that the reduction of oxyhæmoglobin by ammonium sulphide is facilitated by the catalase of blood. If this is destroyed, however, by boiling, the liquid still retains the power of accelerating reduction. When the reduced hæmoglobin is shaken with air, re-oxidation occurs, and the process can be repeated a certain number of times until the pigment is destroyed. It has been found, however, that the alternate reduction and oxidation can be repeated indefinitely if, instead of ammonium sulphide, a maceration of Roquefort cheese is used after it has been allowed to grow a bacterial flora by exposure to air. A species of *Coccus* has been isolated from this culture, and found to have a strong reducing action on oxyhæmoglobin. W. O. W.

Changes in Physical Condition of Colloids. XI. Imbibition by Gelatin in Acids and Bases. Richard Chiari (*Biochem. Zeitsch.*, 1911, **33**, 167—181).—The experiments were carried out with gelatin, which had been freed from electrolytes by prolonged washing with conductivity water. The plates of gelatin thus treated were exposed to the action of acids and bases, and the amount of water imbibed or lost was determined by weighing the plates. In this way the imbibition grade was determined. If gelatin is purified in the above-mentioned manner, it is extremely sensitive, as regards its imbibition qualities, to acids and bases. A concentration can be determined, in the presence of acids, at which, instead of imbibition, there is a loss of water. The maximum for this loss lies at the isoelectric point of gelatin at $2 \cdot 10^{-5} n$. Acids of different strength, in isohydric concentrations, cause a greater imbibition the smaller their dissociation constant is; thus acetic acid > lactic acid > hydrochloric acid. The deviation of trichloroacetic and sulphuric acids from this rule may be ascribed to the small ionisation of their protein salts, as deduced from viscosity determinations with other proteins. Analogous results were obtained with bases, the weaker bases causing greater imbibition than the stronger bases in isohydroxylic solutions. Amphoteric electrolytes cause smaller imbibition than acids with the same dissociation constants. Theoretical explanations of the results are given, based on Pauli's conception that neutral proteins have a smaller capacity of forming hydrated aggregates than protein salts. S. B. S.

Diastases. I. IVAR BANG (*Biochem. Zeitsch.*, 1911, **32**, 417—442).—Ptyalin, after prolonged dialysis, still retains its diastatic power, although very much weakened. This fact can be demonstrated when the reducing sugar is estimated by the author's method. After adsorption by starch, and washing by centrifugalisation the adsorption-product, the ptyalin is still diastatically active. The addition of sodium chloride to the dialysed ptyalin increases its diastatic action. The optimum action of this salt takes place when the quantities added are of about the same order as those found in saliva. The addition of relatively very much larger quantities of sodium chloride does not, however, reduce to any very large extent the diastatic action. Nitrate and sulphate exert a very much less marked action. Disodium hydrogen phosphate also inhibits the action, which can be entirely destroyed if the saliva is dialysed after treatment with the phosphate. The action can, however, be restored again by addition of chloride. This action is explained by assuming that dialysis of saliva does not entirely remove the chloride; if phosphate is added, however, the pytalin-chloride compound is converted into the corresponding phosphate, and subsequent dialysis then removes all the chloride. Monosodium phosphate in small quantities inhibits only slightly the action of undialysed saliva, but in large quantities it acts strongly; it reactivates dialysed saliva when in small quantities, but to a smaller extent than the chloride; in larger quantities its action again is inhibitory, and this is probably due to the larger hydrogen ion concentration which inhibits ptyalin. This action can be antagonised by addition of the disodium phosphate. Sodium chloride does not act as an activator in presence of lecithin, whereas disodium phosphate does. The monosodium salt acts in the same way as in absence of lecithin. Experiments on the action of saliva under similar conditions to the above (on soluble starch) were carried out on glycogen. In this case the monosodium phosphate was found to exert a strong activating action.

S. B. S.

Influence of the Viscosity of the Medium on Diastatic Activity. PIERRE ACHALME and M. BRESSON (*Compt. rend.*, 1911, **152**, 1328—1330).—A close parallelism has been found to exist between the curves showing for aqueous glycerol solutions, (*a*) variations in the viscosity of the liquid with concentration, and (*b*) the variations in the rate of hydrolysis of sucrose by invertase at different concentrations of glycerol. The rate of hydrolysis diminishes as the viscosity of the medium increases. Similar results were obtained with emulsin, amylase, trypsin, and organic and inorganic oxydases. That the parallelism is not dependent on the chemical nature of the substance causing viscosity is shown by the fact that mannitol acts in the same way. W. O. W.

Rôle of Viscosity in Variations of the Action of Invertase According to the Concentration of Sucrose. PIERRE ACHALME and M. BRESSON (*Compt. rend.*, 1911, **152**, 1420—1422. Compare preceding abstract).—A curve showing the variation in viscosity of a sucrose solution with concentration is almost parallel to the curve showing the time necessary for invertase to hydrolyse a definite percentage of the sugar. W. O. W.

Viscosity and Diastatic Actions. Hypothesis on the Nature of Diastases. PIERRE ACHALME (*Compt. rend.*, 1911, 152, 1621—1624. Compare preceding abstracts).—A theoretical paper. The author is led to regard an enzyme in colloidal solution as composed of granules undergoing Brownian movements, and in consequence losing energy as electrons or vibrations in the ether. When the speed of the electrons or the period of the vibrations corresponds with the intramolecular vibration of a substance capable of being acted on by the enzyme, phenomena of resonance occur, bringing about disruption in a similar way to that produced by ultra-violet light. The specific nature of an enzyme depends on accordance of the radiations with the nature of the passive substance. W. O. W.

Action of Heat on Emulsin. GABRIEL BERTRAND and ARTHUR COMPTON (*Compt. rend.*, 1911, 152, 1518—1521).—Amygdalin was heated for fifteen hours at different temperatures with emulsin. The curve representing the amount of hydrogen cyanide liberated at each temperature is found to be superposable on the curve showing the amount of dextrose, the optimum temperature in each case being about 40°. The curves are no longer superposable, however, if the heating is limited to two hours; the two optimum temperatures under these conditions are 58° and 56° respectively. These observations are held to confirm the view that two distinct diastases are concerned in the hydrolysis of the glucoside, one changing it into a diose and a nitrile, whilst the other effects only fission of the diose. The curves differ from those given by cellase, and hence this also is a specific enzyme, different from the two foregoing (compare Abstr., 1900, i, 290, 800). W. O. W.

Is the So-called Peroxydase Actually a Ferment? HESSE and W. D. KOOPER (*Zeitsch. Nahr. Genussm.*, 1911, 21, 385—393).—The results of the authors' experiments lead them to the conclusion that the coloration obtained when milk is treated with Rothenfusser's reagent (guaiacum, *p*-phenylenediamine hydrochloride, and alcohol) is not due to peroxydase, but solely to the presence of alkaline substances in the milk. As soon as the alkaline reaction of these substances is affected by the addition of acids, or mercuric chloride, or by boiling the milk, the latter does not give a coloration with the reagent. When the added acid is neutralised, a coloration is again obtained. The authors have not ascertained definitely whether the alkaline substances consist of calcium-casein compounds or phosphates; probably several substances are present which produce the effect.

W. P. S.

The Inhibitory Action of Inorganic Salts on Catalase. W. FAVRE (*Biochem. Zeitsch.*, 1911, 33, 32—48).—The influence of the following salts on the action of the catalase of the blood was investigated: sodium chloride and sulphate, potassium chloride and sulphate, magnesium chloride and sulphate, copper chloride and sulphate, ferrous chloride and sulphate, manganese chloride and sulphate; the action of colloidal silver was also investigated. From

the amount of hydrogen peroxide decomposed by the salts, etc., alone and in the presence of catalase, the action of the salts on the catalase itself was determined. S. B. S.

Derivatives of *p*-Aminophenylarsine Oxide. ALFRED BERTHEIM (*Ber.*, 1911, **44**, 1070—1075. Compare Ehrlich and Bertheim, Abstr., 1910, i, 451).—p-*Aminophenylarsine dichloride hydrochloride*, $NH_2\cdot C_6H_4\cdot AsCl_2,HCl$, m. p. 139—140°, is obtained by adding a solution of *p*-aminophenylarsine oxide in cold 2*N*-hydrochloric acid to strongly cooled hydrochloric acid, D 1·19. The corresponding *dibromide*, $NH_2\cdot C_6H_4\cdot AsBr_2,HBr$, m. p. 134°, and *di-iodide*, $NH_2\cdot C_6H_4\cdot AsI_2,HI$, are prepared in a similar manner; the latter, a yellow, crystalline powder, forming a colourless solution in water, is also obtained by reducing arsanilic acid with hydriodic acid. All three substances volatilise almost without residue, yielding crystalline sublimates (probably compounds of aniline and the arsenic trihalogenide) which are decomposed by water into aniline, arsenious acid, and the halogen acid.

p-*Acetylaminophenylarsine oxide*, $NHAc\cdot C_6H_4\cdot AsO$, exists in two forms. The one, indistinctly crystalline, anhydrous, and sparingly soluble, is obtained by reducing acetylarsanilic acid by hydriodic and sulphurous acids, and has m. p. 288—289° (decomp.). The other, obtained by the action of acetic anhydride on an aqueous suspension of *p*-aminophenylarsine oxide, is crystalline and soluble, contains H_2O, and melts partly at 100° (decomp.), completely at 271°. The anhydrous form is converted into the hydrated form by solution in 2*N*-sodium hydroxide, acidifying with 2*N*-acetic acid, and inoculating the solution with a crystal of the hydrated form. p-*Acetylaminophenylarsine dichloride hydrochloride*, $2NHAc\cdot C_6H_4\cdot AsCl_2,HCl$, m. p. 137° (decomp.), is obtained by the action of phosphorus trichloride on a suspension of acetylarsanilic acid in ethyl acetate; from its solution in sodium hydroxide, acetic acid precipitates the hydrated form, and ammonium chloride the anhydrous form of *p*-acetaminophenylarsine oxide. C. S.

Reduction Products of Arsanilic Acid and its Derivatives. II. *pp'*-Diaminoarsenobenzene. PAUL EHRLICH and ALFRED BERTHEIM [and, in part, E. SCHMITZ] (*Ber.*, 1911, **44**, 1260—1269. Compare Abstr., 1910, i, 451).—Arsanilic acid can be reduced directly to the corresponding arseno-derivative, *pp'*-diaminoarsenobenzene,

$$NH_2\cdot C_6H_4\cdot As{:}As\cdot C_6H_4\cdot NH_2,$$

by means of the following reducing agents: (1) Sodium hyposulphite; (2) stannous chloride, alone or in the presence of hydriodic acid as catalyst. An alternative method is to reduce the arsanilic acid to *p*-aminophenylarsine oxide (*loc. cit.*), and then to reduce this to the arseno-derivative by means of sodium amalgam, stannous chloride, and hydrochloric acid or sodium hyposulphite. As a rule, the indirect method of reduction yields a purer product. Derivatives of quinquevalent arsenic are more difficult to reduce than those of tervalent arsenic; thus arsenic acids react slowly with a warm solution of sodium hyposulphite or of stannous chloride, whereas the correspond-

ing arsine oxide even in the cold gives an immediate precipitate of the arseno-derivative. This reaction can be made use of for distinguishing between organic arsinic acids and arsine oxides. The arseno-compounds cannot be distilled; many possess colloidal properties. They are extremely reactive, and many undergo rapid oxidation on exposure to the air.

pp′-*Diaminoarsenobenzene*, $C_{12}H_{12}N_2As_2$, has m. p. 260°, and is insoluble in most solvents, with the exception of acetic acid and pyridine. It possesses basic properties and yields a *hydrochloride*, $C_{12}H_{12}N_2As_2,2HCl$, which decomposes at 151°, and a sparingly soluble *sulphate*. It reduces ammoniacal solutions of silver nitrate in the cold, and is readily oxidised by alkaline hydrogen peroxide or by an acetic acid suspension of iodine to aminophenylarsinic acid. The arseno-compound can be diazotised, and the resulting diazo-salt coupled with phenols to azo-dyes. It also yields condensation products with aldehydes and β-naphthaquinonesulphonic acid. When warmed with acids, the arseno-compounds yield strongly coloured products.

The *sulphite*, $2C_{12}H_{12}N_2As_2,H_2SO_3$, forms a yellow precipitate, very sparingly soluble in the usual solvents.

p-Aminophenylarsine oxide and *pp*′-diaminoarsenobenzene have pronounced toxic properties. In the case of rabbits the former is the more active. J. J. S.

Preparation of a Nitro-1-aminophenyl-4-arsinic Acid. FARBWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D. R.-P. 231969).—*Oxanil*-4-*arsinic acid*, $CO_2H{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}AsO(OH)_2$, a crystalline powder, is prepared by heating sodium *p*-aminophenylarsinite (347 parts) with crystalline oxalic acid (378 parts) at 120—130° and subsequently at 160°. When dissolved in concentrated sulphuric acid and treated with nitric acid (D 1·4) in the same solvent (at a temperature not exceeding 20°), it yields a crystalline paste of *nitro-oxanil*-4-*arsinic acid*; this is converted by boiling water into *nitro*-1-*aminophenyl*-4-*arsinic acid*, yellow needles, which separate as the solution cools. F. M. G. M.

Preparation of Soluble Compounds from Hydroxymercuricarboxylic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 229574, 229575, 229781. Compare Abstr., 1910, i, 347, 459).—When sodium diethylbarbiturate is treated with hydroxymercuribenzoic anhydride in aqueous solution and the mixture evaporated, it yields a crystalline neutral *compound*. The *product* from hydroxymercuri-*o*-chlorobenzoic anhydride and glutarimide is also crystalline, and the reaction is stated to be applicable to other metals, such as lithium and sodium.

The second and third patents record the preparation of soluble crystalline, double *compounds* from hydroxymercuri-*m*-hydroxybenzoic anhydride with acetamide, and with alanine; and from hydroxymercuribenzoic anhydride with caffeine, and with asparagine. These products are decomposed by concentrated hydrochloric acid with separation of mercurous chloride. F. M. G. M.

Complex Mercury Compounds of Cinnamic Acid and its Esters. WALTHER SCHRAUTH, WALTER SCHOELLER, and RICHARD STRUENSEE (*Ber.*, 1911, **44**, 1048—1057).—By the use of various alcohols and esters of cinnamic acid, the following complex mercury compounds, and the internal anhydrides obtained therefrom by hydrolysis, have been prepared by the methods already described (Abstr., 1910, i, 347) in order to show that the reaction follows the course previously suggested. *Methyl α-acetoxymercuri-β-ethoxy-β-phenylpropionate*, $OEt\cdot CHPh\cdot CH(CO_2Me)\cdot Hg\cdot OAc$, m. p. 123° (corr.), long needles, forms a *mercurichloride*, $C_{12}H_{15}O_3HgCl$, m. p. 114°, *mercuribromide*, m. p. 85°, and *mercuri-iodide*, m. p. 71°, and yields by hydrolysis the internal *anhydride*, $OEt\cdot CHPh\cdot CH<\begin{matrix}CO_2\\|\\Hg\end{matrix}$, decomp. 191° (corr.). *Methyl α-acetoxymercuri-β-propoxy-β-phenylpropionate*, $C_{15}H_{20}O_5Hg$, m. p. 135·5° (corr.), forms a *mercurichloride*, m. p. 109°, *mercuribromide*, m. p. 84°, *mercuri-iodide*, m. p. 84°, and an internal *anhydride*, decomp. 188° (corr.). *Methyl α-acetoxymercuri-β-*iso*propoxy-β-phenylpropionate*, m. p. 150° (corr.), yields the internal *anhydride*, $C_{12}H_{14}O_3Hg$, decomp. 191° (corr.). *Methyl α-acetoxymercuri-β-*iso*butoxy-β-phenylpropionate*, m. p. 154° (corr.), yields the internal *anhydride*, $C_{13}H_{16}O_3Hg$, decomp. 193° (corr.). *Ethyl α-acetoxymercuri-β-methoxy-β-phenylpropionate*, m. p. 107°, and *benzyl α-acetoxymercuri-β-methoxy-β-phenylpropionate*, m. p. 127°, have also been prepared.

A methyl-alcoholic solution of mercuric acetate reacts with allyl cinnamate to form a soluble mercuriacetate, which is precipitated by aqueous sodium chloride as the *dimercurichloride*,

$$OMe\cdot CHPh\cdot CH(HgCl)\cdot CO_2\cdot CH_2\cdot CH(OMe)\cdot CH_2\cdot HgCl,$$

m. p. 169° (decomp.).

The internal anhydride of α-hydroxymercuri-β-methoxy-β-phenylpropionic acid (*loc. cit.*) is moistened with alcohol, suspended in water, and brought into solution by the addition of potassium iodide; by acidifying the solution with *N*-sulphuric acid, a *substance*, $C_{18}H_{16}O_5Hg$, m. p. 200° decomp.), is obtained, which acts as a dibasic acid and does not yield mercuric sulphide by treatment with ammonium sulphide. Probably it has the constitution

$$O<\begin{matrix}CHPh\cdot CH(CO_2H)\\CHPh\cdot CH(CO_2H)\end{matrix}>Hg,$$

C. S.

Stannous Alkyl Derivatives. I. PAUL PFEIFFER (*Ber.*, 1911, **44**, 1269—1274. Compare Löwig, *Annalen*, 1852, **84**, 320; Frankland, *ibid.*, 1853, **85**, 329).—[With R. PRADE.]—Pure tin diethyl is most readily prepared by reducing tin diethyl chloride with 4% sodium amalgam and ether, and filtering rapidly, all the work being carried on in an atmosphere of hydrogen. It forms a pale yellow, odourless oil, and decomposes when distilled under reduced pressure. It combines readily with oxygen, yielding a white, amorphous precipitate of the oxide, $SnEt_2O$. It also combines readily with chlorine, bromine, or iodine, and with ethyl iodide at 140° yields tin triethyl iodide.

[With H. REKATE.]—Nearly pure tin diethyl can be obtained by

the action of a large excess of magnesium ethyl bromide on stannous chloride, provided the Grignard reagent is free from alkyl iodide.

J. J. S.

Hexaphenylsilicoethane and Some Biphenyl-substitution Products of Ordinary Ethane and Ethylene. WILHELM SCHLENK, JULIUS RENNING, and GEORG RACKY (*Ber.*, 1911, 44, 1178—1182).—The action of metals on triphenylsilicyl chloride has been investigated, in the hope of obtaining the silicon analogue of triphenylmethyl.

The metals usually employed for the removal of halogen in the preparation of triphenylmethyl are without action on triphenylsilicyl chloride. The removal of chlorine from the latter compound may, however, be effected by heating it with sodium in xylene solution. The *hexaphenylsilicoethane*, $SiPh_3 \cdot SiPh_3$, thus obtained, crystallises in slender prisms, m. p. about 354°. It shows no tendency to dissociate, and remains unchanged when subjected to the action of oxygen in hot xylene solution. From its stability the conclusion is drawn that the total valency of the silicon atom is greater than that of the carbon atom.

Triphenylsilicyl chloride does not form coloured additive products, and remains colourless in contact with phenol. The *sodium* derivative of triphenylsilicol is obtained in a crystalline condition by heating the silicol with sodium in toluene solution.

It has previously been shown that the introduction of phenyl groups into hexaphenylethane greatly increases the tendency to dissociation. In order to ascertain if a similar influence is to be observed in the case of tetraphenylethane and tetraphenylethylene, the authors have prepared and examined the behaviour of some tetraphenyl derivatives of these hydrocarbons; no evidence of dissociation was obtained.

ω-Bromo-di-4-diphenylmethane, $CHBr(C_6H_4Ph)_2$, prepared by brominating di-4-diphenylmethane (Weiler, this Journ., 1875, 151) at 185°, crystallises in colourless leaflets, m. p. 143; it gives a red (in thin layers, blue) coloration with strong sulphuric acid, and is converted by aqueous potassium hydroxide into *di*-p-*phenylbenzhydrol*, $CH(C_6H_4Ph)_2 \cdot OH$, leaflets or needles, m. p. 150°. When heated with copper-bronze in xylene solution, it yields s-*tetra*-4-*diphenylethane*, $CH(C_6H_4Ph)_2 \cdot CH(C_6H_4Ph)_2$. This forms short prisms, m. p. 276—279°, and crystallises from benzene and xylene with one molecule of the solvent. Its solutions in solvents of high boiling point are colourless, do not decolorise iodine, and are unattacked by oxygen, so that no dissociation takes place. *Tetra*-4-*diphenylethylene*, $C(C_6H_4Ph)_2 : C(C_6H_4Ph)_2$, prepared by heating ω-bromodi-4-diphenylmethane above its melting point, crystallises in pale yellow needles, m. p. 330°.

F. B.

Organic Chemistry.

$\Delta^{a\kappa}$-Undecadiene and Δ^{ao}-Hexadecadiene. J. N. Reformatsky, E. Grischkewitsch-Frochimowsky, and A. Semenzoff (*Ber.*, 1911, **44**, 1885—1886).—A mixture of undecadiene and hexadecadiene is obtained on adding magnesium ribbon to $a\epsilon$-dibromopentane in ethereal solution, and subsequently boiling with allyl bromide. The hydrocarbons were fractionally distilled under reduced pressure over metallic sodium.

$\Delta^{a\kappa}$-*Undecadiene*, $C_{11}H_{20}$, is a colourless, mobile liquid, b. p. 187°/755 mm. (corr.), D^{20} 0·7671, n_D^{20} 1·43497. It decolorises 4 atoms of bromine in ethereal solution, forming a viscid, colourless tetrabromide.

Δ^{ao}-*Hexadecadiene*, $C_{16}H_{30}$, is a colourless, mobile liquid, solidifying to a mass of crystalline leaflets, m. p. −14° to −12°, b. p. 142—147°/6 mm., D_4^{18} 0·8149, n_D^{18} 1·45612. It forms a viscid, faintly red-coloured tetrabromide.

Both hydrocarbons form bright green additive products with liquid nitrogen trioxide. $\Delta^{a\delta}$-Dodecadiene and dimethyldodecadiene have been prepared in a similar manner. E. F. A.

Preparation of Chloro- and Bromo-compounds from Organic Bases. Julius von Braun and W. Sobecki (*Ber.*, 1911, **44**, 1464—1475. Compare Abstr., 1904, i, 731, 841; 1905, i, 206, 341, 596, 634; 1907, i, 79; 1910, i, 25, 119).—A simple method for the preparation of an alkyl chloride, RCl, from an amine, $R{\cdot}NH_2$, is to benzoylate the amine and to decompose this according to the equation: $R{\cdot}NH{\cdot}COPh + PCl_5 = POCl_3 + PhCN + RCl$. This reaction does not proceed quantitatively, and only 60—75% of benzonitrile is formed as a rule. After removing the phosphoryl chloride by means of water, the benzonitrile and alkyl chloride can be separated in certain cases by fractional distillation. If, however, the boiling points are too close for such a separation, the mixture is treated with a slight excess of ethyl alcohol and one equivalent of hydrogen chloride, and on the addition of ether the crystalline benzimino-ethyl ether hydrochloride is completely precipitated at the end of four days.

The following compounds have been prepared by this method: ϵ-Phenylamyl chloride, 73% (Abstr., 1910, i, 844); $a\eta$-dibromoheptane, 65% (Abstr., 1906, i, 577), and $a\epsilon$-dichloropentane. The method is much more convenient than the old one of removing the benzonitrile by hydrolysis to benzoic acid. Nonyl bromide is readily obtained from octyl iodide, by converting the latter into the cyanide, reducing with sodium and alcohol to nonylamine, and then treating according to the general method. Nonylamine has b. p. 201°, and rapidly absorbs moisture and carbon dioxide (compare Hofmann, Abstr., 1882, 1054). It is not identical with the nonylamine prepared from petroleum by Pelouze and Cahours (*Jahres.*, 1863, 529). The *hydrochloride* crystallises well and is not hygroscopic; the *platinichloride*, $C_{18}H_{44}N_2Cl_6Pt$, forms a pale yellow precipitate, and decomposes at 205—207°; the

picrate, $C_{15}H_{24}O_7N_4$, crystallises from alcohol in brilliant needles, m. p. 111°, and the *benzoyl* derivative, $C_{16}H_{25}ON$, is readily soluble in alcohol and has m. p. 49°. *Nonyl bromide*, $C_9H_{19}Br$, is a colourless liquid, b. p. 91°/9 mm. With magnesium and carbon dioxide in the presence of dry ether, it yields decoic acid together with octadecane.

Pentadecyl chloride can be obtained from palmitic acid by transforming the latter into its amide, and conversion of this into pentadecylamine, the *benzoyl* derivative of which has m. p. 78°. *Pentadecyl chloride*, $C_{15}H_{31}Cl$, is an oil with b. p. 168—171°/10 mm., and on treatment with aniline yields pentadecylaniline (Le Sueur, Trans., 1910, **97**, 2433).

Heptadecyl chloride can also be obtained from cetyl iodide by conversion into the nitrile, reduction of this with sodium and alcohol, and treatment of the benzoyl derivative of the resulting amine with phosphorus pentachloride. *Cetyl cyanide* [*heptadeconitrile*], $C_{16}H_{33}\cdot CN$, has b. p. 208°/10 mm., and m. p. 29°. Heptadecylamine has b. p. 322—324° and m. p. 48°, and *heptadecyl chloride*, $C_{17}H_{35}Cl$, b. p. 192—195°/10 mm. and m. p. 24°.

$\alpha\mu$-Dichlorododecane can be obtained from $\alpha\kappa$-di-iodododecane (Abstr., 1910, i, 26) by a similar method. When the dibenzoyl derivative of $\alpha\mu$-diaminododecamethane (*loc. cit.*) is distilled with phosphorus pentachloride under reduced pressure, and the products decomposed with water, *$\alpha\mu$-dichlorododecane*, $C_{12}H_{24}Cl_2$, is obtained as an oil, b. p. 170—172°/10 mm., which solidifies and then has m. p. 29°. With sodium phenoxide and alcohol it yields $\alpha\mu$-diphenoxydodecane, m. p. 86°. A by-product obtained during the distillation of the dichloro-derivative is *μ-chlorododecylbenzamide*, $CH_2Cl[CH_2]_{11}\cdot NH\cdot COPh$, which crystallises from a mixture of ether and light petroleum in brilliant plates, m. p. 66°. J. J. S.

Preparation of Olefine Alcohols of the General Formula $OH\cdot CHMe\cdot CR{:}CH_2$. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 233519).—It is found that unsaturated $\alpha\beta$-ketones can be readily converted into the therapeutically valuable olefine alcohols of the general formula $OH\cdot CHMe\cdot CR{:}CH_2$ (where R is hydrogen or an alkyl group) by a series of operations represented by the following equations:

(1) $COMe\cdot CR{:}CH_2 + NHMe_2 = COMe\cdot CHR\cdot CH_2\cdot NMe_2$.

(2) $COMe\cdot CHR\cdot CH_2\cdot NMe_2 + H_2 = OH\cdot CHMe\cdot CHR\cdot CH_2\cdot NMe_2$,

this on methylation and subsequent treatment with silver hydroxide yields $OH\cdot CHMe\cdot CHR\cdot CH_2\cdot NMe_3\cdot OH$, which is readily decomposed by heat into water, trimethylamine, and the required alcohol.

β-Methyl-Δ^{α}-buten-γ-ol, $OH\cdot CHMe\cdot CMe{:}CH_2$, a colourless oil, b. p. 113—115°, sparingly soluble in water, which on oxidation with chromic acid yields the characteristic odour of ethyl vinyl ketone, was obtained by means of the following intermediate compounds: β-Methyl-Δ^{α}-buten-γ-one, $COMe\cdot CMe{:}CH_2$, was converted by dimethylamine into *dimethyl-β-acetylpropylamine*, $CHMeAc\cdot CH_2\cdot NMe_2$, b. p. 51—51·5°/13 mm., a colourless oil readily soluble in water; this on reduction with sodium amalgam or electrolysis yielded *δ-dimethylamino-γ-methylbutan-β-ol*, $OH\cdot CHMe\cdot CHMe\cdot CH_2\cdot NMe_2$, a colourless, soluble

oil, b. p. 64—66°/16 mm., or 166—167° under atmospheric pressure; the *methiodide*, m. p. 154°, furnished, on treatment with silver hydroxide, a syrupy *base*, which decomposed at 140—160° into the required *β-methyl-Δ^{a}-buten-γ-ol*. Methyl vinyl ketone, $CH_3\cdot CO\cdot CH{:}CH_2$, on treatment with dimethylamine yielded *δ-dimethylamino-β-butanone*, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot NMe_2$, b. p. 39—45°/14 mm., a colourless oil readily soluble in water, which on reduction furnished *δ-dimethylamino-β-butanol*, $OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot NMe_2$, b. p. 150—155°, a soluble oil with an odour of piperidine, and was subsequently converted into *methylvinylcarbinol*, $OH\cdot CHMe\cdot CH{:}CH_2$, b. p. 98—100°, a colourless oil sparingly soluble in water. F. M. G. M.

Beeswax. III. Are the Alcohols from Psyllawax and Beeswax Identical? ERNST EDW. SUNDWIK (*Zeitsch. physiol. Chem.*, 1911, 72, 455—458. Compare Abstr., 1899, i, 112; 1907, i, 887).—It is shown that the alcohol from beeswax is not identical with psylla alcohol. When the latter is heated with soda-lime at 360—370°, psyllic acid is formed, whereas the same acid cannot be obtained from the alcohol of beeswax.

Beeswax alcohol and soda lime at 320° yield a compound containing C = 84·05 and H = 14·60%; $(C_{33}H_{67})_2O$ or $(C_{32}H_{65})_2CO$? It crystallises from acetone, has m. p. 56—56·5°, and b. p. 310—314°. The alcohol and soda lime at 220—260° yield a small amount of an *acid* with m. p. 78°. The *silver* salt gave Ag = 17·53%. J. J. S.

Acid Sodium Acetates. RYUJI ABE (*Mem. Coll. Sci. Eng. Kyōtō*, 1911, 3, 13—17. Compare Vaselieff, Abstr., 1909, i, 756).—The solubility of sodium acetate in acetic acid solutions at 20° has been determined, also the composition of the residues, and the conditions under which the hydrated salt as well as the acid salts come into existence found to be as follows:

Molecular percentage in solution.		Residue.
$NaC_2H_3O_2$.	$C_2H_4O_2$.	
9·5	0	$NaC_2H_3O_2,3H_2O$.
10·82	8·28	$NaC_2H_3O_2,C_2H_4O_2$.
10·84	32·90	$NaC_2H_3O_2,2C_2H_4O_2$.
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J. D. K.

Solubility of Strontium Acetate and the Transition Point of its Hydrates. YUKICHI OSAKA and RYUJI ABE (*Mem. Coll. Sci. Eng. Kyōtō*, 1911, 3, 51—54).—Strontium acetate is well known to crystallise with $\frac{1}{2}H_2O$ at 15°, but with $4H_2O$ at lower temperatures. The solubility has been determined between 0° and 97°, and the transition point found to be 9·4°. Above this temperature the solubility decreases, and seems to reach a minimum at about 83°. The crystals, stable at lower temperatures, were difficult to free completely from the mother liquor on account of their instability at the ordinary temperature. A small quantity of strontium chloride was therefore

added to the solution, and the amount of mother liquor adhering to the crystals taken for analysis was estimated from their chloride content. J. D. K.

Catalytic Preparation in the Wet Way of Esters of Saturated Aliphatic Acids. JEAN B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1911, **152**, 1671—1673. Compare Abstr., 1910, i, 649, 651).—Two hundred c.c. of a mixture of acetic acid and alcohol in equimolecular proportions give on distillation a liquid containing 17·8% of the theoretical amount of ethyl acetate, whereas under the same conditions, but in presence of 10 grams of anhydrous aluminium sulphate or potassium hydrogen sulphate, the yield of ester is 82%. With 1% of sulphuric acid by volume, the yield is 86·5%. The catalytic effect of the latter is attributed to the formation of ethyl hydrogen sulphate; this becomes converted into the relatively unstable ethyl sulphate, which reacts with acetic acid to form the ester and ethyl hydrogen sulphate. The latter is the actual catalyst and not the sulphuric acid. Anhydrous sodium sulphate is without catalytic effect on esterification, and hence the reaction is not entirely dependent on the efficiency of the catalyst as a dehydrating agent.

W. O. W.

Ethyl Acetate. A. KURTENACKER and H. HABERMANN (*J. pr. Chem.*, 1911, [ii], **83**, 541—552).—Continuing the experiments of Habermann and Brezina (Abstr., 1909, i, 873), the authors have investigated the formation of ethyl acetate from 96 volume % alcohol and glacial acetic acid in the presence of sodium metaphosphate, or the ignited sulphate of copper, magnesium, nickel, zinc or sodium as the dehydrating agent. A mixture of the alcohol and the acid in approximately molecular proportions is kept for some hours with a quantity of the dehydrating agent in excess of that required to combine with the water produced in the reaction; the whole is then heated for many hours under a reflux condenser, the course of the reaction being followed by siphoning off samples at intervals, cooling, filtering, and titrating the residual acetic acid with $N/2$-sodium hydroxide. Sodium metaphosphate or sodium sulphate has no influence whatever on the yield of ethyl acetate; copper sulphate, zinc sulphate, and magnesium sulphate produce approximately the same effect; nickel sulphate is by far the best dehydrating agent. Having shown that an excess of alcohol or the prolonged heating of the mixture does not improve the yield of purified ethyl acetate, the authors state the following as the best conditions for the preparation of the ester.

A mixture of 200 grams of alcohol, 250 grams of acetic acid, and about 160 grams of anhydrous nickel sulphate is distilled until the temperature begins to exceed 73°. The condenser is then arranged vertically, and the mixture is heated under reflux, until the b. p. has fallen below 73°. The condenser is then reverted, and the mixture again distilled until the temperature begins to exceed 73°. These operations are repeated as long as any liquid distils over below 73°. The distillate containing a molecular compound of ethyl alcohol and ethyl acetate, b. p. about 72° (*loc. cit.*), is purified in the usual way.

C. S.

Preparation of Esters of Organic Acids with the Exception of those of Formic Acid. ADMINISTRATION DER MINEN VON BUCHSWEILER AKT.-GES. (D.R.-P. 232818).—It is found that esters can be prepared in quantitative yield by boiling the components together in the presence of anhydrous calcium chloride and a mineral acid; the ester rises to the surface of the liquid, and is thus readily separated from the hydrated calcium chloride. Details for the preparation of ethyl and amyl acetates, methyl butyrate, ethyl benzoate, and ethyl phthalate are given in the patent. F. M. G. M.

Preparation of Tri-iodo-derivatives of Stearic Acid. ERNST ERDMANN (D.R.-P. 233893).—Tri-iodostearic acid derivatives may be obtained by the action of three molecules of iodine monobromide or monochloride or hydrogen iodide in acetic acid on a cooled solution of linoleic acid in the same solvent; excess of halogen is removed with sulphurous acid, the product separated by stirring in petroleum, and then crystallised from acetic acid.

Tribromotri-iodostearic acid has m. p. 122—124°, and by shaking with calcium hydroxide is converted into its *calcium* salt.

Trichlorotri-iodostearic acid is a colourless, crystalline powder, m. p. 144°.

Tri-iodostearic acid is obtained when hydrogen iodide is employed, and forms a *calcium* salt. F. M. G. M.

Preparation of Unsaturated Dihalogenated Aliphatic Acid Chlorides. F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 232459).—It is found that the hitherto unknown unsaturated dihalogenated aliphatic acid chlorides of the general formula $C_nH_{2n-4}X_2O_2$ (X = halogen) can be prepared in quantitative yield by the action of thionyl chloride on the corresponding dihalogenated acid.

Di-iodostearolyl chloride is thus obtained from di-iodostearolic acid (Liebermann and Sachse, Abstr., 1892, i, 470); it forms a yellow oil, which can be distilled under 0·3 mm. pressure without decomposition; the corresponding *dibromostearolyl chloride* is a pale brown, oily fluid, which solidifies at the temperature produced by a mixture of solid carbon dioxide and ether.

Di-iodotaririolyl chloride forms brownish-yellow, spear-shaped crystals, m. p. 28°.

Di-iodobehenolyl chloride has m. p. 19°. F. M. G. M.

Preparation of Stable Bromo- and Iodo-derivatives of Fats Free from Sulphur. ARNOLD VOSWINKEL (D.R.-P. 233857).—Animal and vegetable oils can be conveniently halogenated in alcoholic solution by means of the reaction occurring between chloral hydrosulphide and bromine (or iodine) according to the equation $(C_2HCl_3O)_2,H_2S + 2I = 2HI + S + 2C_2HCl_3O$, when the halogen acid formed at once attacks the oil.

Sesame oil under these conditions yielded a yellow, oily *product* containing 4—5% iodine.

Butylchloral hydrosulphide, obtained by passing hydrogen sulphide into a solution of butylchloral in chloroform, forms leaflets, m. p. 85°.

These oils containing bromine and iodine are therapeutically active.

F. M. G. M.

"Alcoholysis" of Japan Wax. Eugène Tassilly (*Bull. Soc. chim.*, 1911, [iv], 9, 608—615. Compare Geitel and van der Want, Abstr., 1900, i, 271, Schaal, Abstr., 1908, i, 3, and Matthes and Heintz, Abstr., 1910, i, 149).—The author has examined the acids furnished by Japan wax when "alcoholysed" by Haller's process (Abstr., 1907, i, 9). It was found necessary to add sufficient ether to keep the material in solution, and under these conditions the process had to be continued thirteen hours to effect complete hydrolysis.

The wax consists principally of palmitin, and by Haller's method a yield of 55% of pure methyl palmitate is readily obtained from it. Other acid constituents detected in the course of the present investigation were pelargonic, stearic, oleic, and japanic acids, and an *acid*, $C_{15}H_{30}O_2$ (or $C_{30}H_{58}O_4$), m. p. 87°, with acids soluble in water and possibly including some *iso*butyric acid. No arachidic acid was found. The unsaponifiable matter amounted to 0·54%. T. A. H.

Keto-enolic Equilibrium of Ethyl Acetoacetate. Arthur Hantzsch (*Ber.*, 1911, 44, 1771—1776).—Correction of mistakes in, and a more extended discussion of, work already recorded (Abstr., 1910, i, 811; compare also Meyer, this vol., i, 351; Knorr, *ibid.*, i, 516). C. S.

Neutralisation Curve of Oxalic Acid. J. E. Enklaar (*Chem. Weekblad*, 1911, 8, 487—492).—A table is given containing the results of measurements with the gas electrode, obtained in the step-by-step neutralisation of solutions of oxalic acid with sodium hydroxide. A curve is appended showing the relation of the concentration of the hydrogen ions to the quantity of added alkali.

A. J. W.

Improved Method of Preparation of Mono-substituted Malonic and Acetoacetic Esters. Hermann Leuchs (*Ber.*, 1911, 44, 1507—1511).—The formation of the disubstituted ethyl malonate, which is usually obtained as a by-product in the preparation of the mono-substituted ester, can be prevented to a great extent by employing a large excess, usually 1 mol., of ethyl malonate. Thus the following substances have been prepared, the figures in the brackets denoting the yield by the ordinary method: ethyl benzylmalonate, 85% (50—55%); ethyl γ-phenoxyethylmalonate, 89% (55%: Fischer and Blumenthal, Abstr., 1907, i, 191); ethyl δ-chloro-γ-valerolactone-α-carboxylate, 78% (50%: Traube and Lehmann, Abstr., 1901, i, 501); ethyl γ-bromopropylmalonate, 35—38% (25%: Willstätter and Ettlinger, Abstr., 1903, i, 362).

Similarly, by using an excess of ethyl acetoacetate, ethyl benzylacetoacetate has been obtained in 89% yield (55%), and acetyl-δ-chlorovalerolactone in 74% yield (50%: Traube, *loc. cit.*).

C. S.

Ethyl Oxalylsuccinate. WILHELM WISLICENUS and MARTIN WALDMÜLLER (*Ber.*, 1911, **44**, 1564—1573).—An ether-alcohol solution of potassium ethoxide reacts with ethyl oxalate to form insoluble ethyl potassio-oxalylsuccinate; this crystallises in very slender, matted needles. On acidifying, the ester is obtained as a colourless oil; it exists in two forms in equilibrium, the enolic, giving a deep red and the ketonic, showing no coloration with ferric chloride. Of the solvents methyl and ethyl alcohols, ether and benzene, the first named contains least, and the last most, of the enolic modification.

With ammonia, ethyl oxalylsuccinate forms a neutral crystalline salt-like additive product, which sinters at 82°, m. p. 88—89°. This substance changes spontaneously, or more quickly on warming, to *ethyl α-amino-β-carboxyglutaconate*,

$$CO_2Et\cdot C(NH_2):C(CO_2Et)\cdot CH_2\cdot CO_2Et.$$

This crystallises in colourless, lustrous plates, m. p. 68—69°, b. p. 255—260°/112 mm. or 211—214°/27 mm.

The ammonia compound interacts with copper acetate, forming *ethyl cupro-oxalylsuccinate*, crystallising in slender, green needles, m. p. 64—69°. The corresponding *nickel* compound forms greenish-white needles, m. p. 114—119°; the *zinc* compound separates in colourless needles.

Ethyl oxalylsuccinate phenylhydrazone separates in small, pale yellow crystals, m. p. 85°. At 150°, or on treatment with hydrogen chloride in ethereal solution, ethyl 3-carboxy-1-phenyl-5-pyrazolone-4-acetate is obtained. This forms an *acetyl* derivative crystallising in colourless needles, m. p. 89—90°. The corresponding acid phenylpyrazolone, obtained by hydrolysis of the ester, is converted by acetyl chloride into the *anhydride* of 3-*carboxy*-1-*phenyl*-5-*acetoxypyrazole*-4-*acetic acid*, $\begin{array}{l}C(O\cdot COMe):C\cdot CH_2\cdot CO\\ | \qquad\qquad\quad | \qquad\quad |\\ NPh\text{——}N:C\text{—}CO\text{—}O\end{array}$, which crystallises in lustrous, colourless needles, m. p. 150—151°.

On boiling with alkali and acidifying, 3-carboxy-1-phenylpyrazolone-4-acetic acid, m. p. 232°, is obtained. On boiling with alcohol and precipitating with water, the mono-*ethyl* ester of the acetylated acid is obtained in colourless, lustrous needles, m. p. 178—182°.

Ethyl oxalylsuccinate forms a crystalline additive product with diphenylhydrazine, m. p. 78—79°; on keeping, this changes into the *diphenylhydrazone*, which is an oil.

With hydroxylamine an *additive product* consisting of 2 mols. of ester and 1 mol. of hydroxylamine is obtained; it crystallises in slender, colourless needless, which soften at 55°, m. p. 61—62°.

α-Ketoglutaric acid forms colourless crystals, m. p. 115—116°; the *diethyl* ester is a colourless liquid, b. p. 160°/23 mm. The *phenylhydrazone* of the acid crystallises in almost colourless plates, m. p. 152—153°; on keeping or when heated, the anhydride, 1-*phenyl*-6-*pyridazinone*-3-*carboxylic acid*, $NPh<\begin{matrix}CO\text{——}CH_2\\ N:C(CO_2H)\end{matrix}>CH_2$, is obtained. It forms colourless plates, m. p. 172°, and the solution in concentrated sulphuric acid is not coloured by either ferric chloride or potassium dichromate.

On the introduction of hydrogen chloride into a warm alcoholic solution of the anhydride, ammonium chloride is eliminated and *ethyl 2-carboxyindole-3-acetate*, $C_6H_4<\genfrac{}{}{0pt}{}{C(CH_2\cdot CO_2Et)}{NH\!-\!-\!-\!-\!-\!-\!-\!-}>C\cdot CO_2Et$, obtained in colourless plates, m. p. 83—84°. E. F. A.

Oxidation of Unsaturated Compounds with Organic Peroxides. II. Oxidation of Derivatives of Unsaturated Hydrocarbons with One Double Linking. NIKOLAUS PRILESCHAEFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 609—620).—It has been already shown that the interaction of hydrocarbons of the series, C_nH_{2n-2}, and benzoylhydroperoxide proceeds according to the scheme: $:C:C: + Ph\cdot CO\cdot O\cdot OH \longrightarrow \genfrac{}{}{0pt}{}{:C}{:C}>O + Ph\cdot CO_2H$ (Abstr., 1910, i, 86; this vol., i, 255). In the present paper it is shown that the oxidation of derivatives of these hydrocarbons, for example, aldehydes, ketones, alcohols, etc., proceeds in the same way.

Thus, allyl alcohol yields the corresponding oxide (glycide) (compare Nef, Abstr., 1905, i, 3), $\genfrac{}{}{0pt}{}{O\!-\!-}{CH_2}>CH\cdot CH_2\cdot OH$.

Oxidation of citronellal (b. p. 103—105°/25 mm., $[\alpha]_D$ +9·79°, D_{16}^{16} 0·8624) gives *citronellal oxide*, $C_{10}H_{18}O_2$, as a colourless liquid, b. p. 126—127°/20 mm., D_0^0 0·9437, D_{16}^{16} 0·9344, $[\alpha]_D$ +9·63°, n_D^{16} 1·44210, which gives all the aldehyde reactions, but does not form a crystalline oxime or semicarbazone. The oxidation proceeds thus: $CMe_2:CH\cdot R + O \longrightarrow CMe_2<\genfrac{}{}{0pt}{}{CH_2R}{O}$ or

$$CH_2:CMe\cdot CH_2\cdot R + O \longrightarrow \genfrac{}{}{0pt}{}{CH_2}{O\!-\!-}>CMe\cdot CH_2R.$$

Citronellal oxide readily undergoes hydration to the *glycol*, $C_{10}H_{20}O_3$, which is a viscous, colourless liquid, b. p. 180—182°/18 mm., and forms an *acetyl* derivative, $C_{10}H_{19}O_3Ac$, b. p. 175—176°/13 mm., D_0^0 1·0418, D_4^{16} 1·0295, n_D^{16} 1·4571. From dihydroxydihydrocitronellaldimethylacetal, Harries and Schauwecker (Abstr., 1901, i, 730) also obtained a dihydroxyaldehyde, but the b. p., 158—162°/22 mm., is appreciably lower than that found for the above glycol.

Methylheptenone, $CMe_2:CH\cdot CH_2\cdot CH_2\cdot COMe$, on oxidation gives:

(1) The *oxide*, $\genfrac{}{}{0pt}{}{CMe_2}{O\!-\!-\!-}>CH\cdot CH_2\cdot CH_2\cdot COMe$, as a mobile, colourless liquid, b. p. 68—70°/50 mm., 146·5—147·5°/746 mm., D_0^0 0·9870, D_4^{16} 0·9718, $n_D^{16·1}$ 1·43031; it is not oxidised by permanganate, reduces Fehling's solution slightly, and does not give a crystalline oxime or semicarbazone. It is readily hydrated, giving the *glycol*,

$$OH\cdot CMe_2\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot COMe,$$

as a mobile liquid, b. p. 139—140°/13 mm., D_0^0 1·0698, D_4^{16} 1·0582, $n_D^{16·2}$ 1·4610, which slowly crystallises; m. p. 65—66°. Dehydration of the glycol yields the *diketone*, $CHMe_2\cdot CO\cdot CH_2\cdot CH_2\cdot COMe$, b. p. 117—119°/50 mm., 94—95°/15 mm., D_0^0 0·9538, D_4^{16} 0·9396, $n_D^{16·2}$ 1·4356, which yields a *dioxime*, m. p. 131·5—132°, and a *monosemicarbazone*. m. p. 197—198°. By oxidising methylheptenone with

permanganate, Harries (Abstr., 1902, i, 345) obtained a glycol, and from this a diketone, both having similar properties to the above.

(2) The *oxide*, $CH_2\!:\!CMe\cdot[CH_2]_3\cdot COMe$ or

$$\begin{array}{l} CH(CHMe_2) \\ | \\ O\text{———————} \end{array}\!\!>CH\cdot CH_2\cdot COMe,$$

b. p. 115—116°/50 mm., D_0^0 0·9963, D_4^{16} 0·9826, $n_D^{16\cdot 3}$ 1·44747. On hydration, it gives a *glycol*,

$$CHMe_2\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot COMe(?),$$

b. p. 143—145°/14 mm., D_0^0 1·0700, D_4^{16} 1·0583, $n_D^{16\cdot 2}$ 1·4599, m. p. 62—63·5°, which is apparently different from the glycol described under (1). It gives, however, the same diketone on dehydration.

T. H. P.

Oxidation of Hexoses by Air in Presence of Alkali Hydroxides. José I. del Rosario (*Revista Filipina Med. Farm.*, 1910, 1, 191).—The oxidation of lævulose by air in presence of alkali hydroxide gives similar products to those obtained by the oxidation of hexoses by Fehling's solution (compare Nef, Abstr., 1898, i, 7; Anderson, Abstr., 1909, i, 881). The oxidation was carried out by bubbling air freed from carbon dioxide through a solution of 100 grams of lævulose in 3500 c.c. of water in which 300 grams of barium hydroxide were dissolved; 1·22 grams of carbon dioxide, 18·3 grams of formic acid, and 77—80 grams of soluble gum were formed. The latter was resolved by Nef's method into glycollic, *d*- and *l*-glyceric, threonic, *d*-mannonic, and *d*-gluconic acids; in addition there was isolated α-hydroxymethyl-*d*-arabonic acid, which was also obtained by Spoehr (Abstr., 1910, i, 221) on oxidising lævulose with hydrogen peroxide in alkaline solution. No lactic, acetic, or oxalic acid was formed.

W. A. D.

Acetohalogen-glucoses and *p*-Bromophenylosazones of Maltose and Melibiose. Emil Fischer (*Ber.*, 1911, 44, 1898—1904. Compare Fischer, Abstr., 1910, i, 716).—An optical inversion takes place when anhydrous liquid hydrogen chloride acts on α-pentacetyldextrose, and β-acetochlorodextrose, $[\alpha]_D$ +160·9° in chloroform, is the main product. The conditions for obtaining α-acetochlorodextrose in this manner have not been again realised (Fischer and Armstrong, Abstr., 1901, i, 257, 671). Similarly, with anhydrous hydrogen bromide, β-acetobromodextrose, $[\alpha]_D$ +199·28° in chloroform, is obtained from α-pentacetyldextrose. β-Acetobromodextrose is conveniently prepared in quantity by the action of anhydrous hydrogen bromide in glacial acetic acid on β-pentacetyldextrose.

The preparation of maltosone from phenylmaltosazone by boiling with benzaldehyde is much facilitated by the presence of 10—15% of benzoic acid in the benzaldehyde.

E. F. A.

Glucodecose and α-Glucodecitol. L. H. Philippe (*Compt. rend.*, 1911, 152, 1774—1776. Compare this vol., i, 12).—Reduction of α-glucodeconic acid, or of the crude mixture of acid and lactone, leads to the production of *α-glucodecose*, $C_{10}H_{20}O_{16}$, m. p. 210°; in aqueous

solution it has $[\alpha]_D$ $+37°$, but after twenty-four hours, or on boiling, shows $[\alpha]_D^{20}$ $+50·4°$. The substance crystallises from water in anhydrous needles, but sometimes separates from concentrated solutions as hexagonal lamellæ containing $1H_2O$. The hydrated form shows the same rotation as the anhydrous substance. The *phenylhydrazone* crystallises in colourless, prismatic needles, m. p. 228—229°; the *osazone* in slender, yellow needles, m. p. 278°.

Further treatment of the decose with sodium amalgam converts it into *a-glucodecitol*, $C_{10}H_{22}O_{10}$, small, prismatic needles, m. p. 222° (sublimes), $[\alpha]_D$ $+1·2°$; the *deca-acetyl* derivative forms rectangular lamellæ, m. p. 149—150°, $[\alpha]_D$ $+16·0°$ in chloroform solution. It combines with benzaldehyde to form an insoluble *acetal*.

W. O. W.

The Solubility of Lime in Solutions of Sucrose. H. Claassen (*Zeitsch. Ver. deut. Zuckerind.*, 1911, 489—509).—To determine the solubility, well-stirred solutions of sucrose were heated with lime at different temperatures for definite intervals of time; the solution was rapidly filtered, and the lime determined in the filtrate, which was also examined polarimetrically.

The solubility of lime in pure solutions of sucrose is independent of the kind of lime when a good commercial sample is used, but it depends on the way in which the lime is added. Most lime dissolves when it is added directly as quicklime, whilst the solubility is the least when an old milk of lime is used. Under the same conditions of experiment the same quantity of lime dissolves.

The solubility increases with the quantity of lime (always in excess) added, until a solubility of 2—2·5% by weight is reached; further increase in the quantity of lime then slightly diminishes the solubility.

Rise in temperature diminishes the solubility, as also does a diminution in the concentration of the sucrose solution. When solutions which have been saturated at 0°, 20°, or 50° are heated in the presence of excess of lime, part of the lime is deposited as such, and not as calcium sucrate. The amount deposited varies with the conditions, but the amount remaining in solution is always greater than that which would be dissolved by direct addition of the lime at the higher temperature.

On warming the filtrates from solutions which have been saturated at 0° or 20°, a deposit is obtained which contains, not only lime, but also calcium sucrate as a gelatinous precipitate. Filtrates from solutions saturated at 50° give practically no deposit on heating to 90—100°.

If sucrose solutions which have been saturated at a high temperature are cooled in the presence of excess of milk of lime, the latter dissolves until the solubility is the same as that which would have been obtained directly at the lower temperature. With quicklime, however, the solubility is less than that obtained directly, but greater than in the case of milk of lime.

Impure sucrose solutions, such as the thin liquor obtained in the

manufacture of sucrose, behave in the same manner as pure solutions of the same sucrose content. T. S. P.

Behaviour of Sucrose, and its Decomposition Products on Heating. J. E. Duschsky (*Zeitsch. Ver. Deut. Zuckerind.*, 1911, 581—608).—As the result of a series of experiments in which the change in the polarisation or in the cupric reducing power was studied, the conclusion is drawn that on heating dextrose either at atmospheric or under increased or reduced pressure, there is no marked increase in the polarisation or reduction in the reducing power. In some cases an increase in the polarisation is observed, indicating the formation of new products; this is due to the use of strong solutions or particularly to the presence of acids, for example, lactic and acetic acids. Lactic acid is particularly active, and in addition prevents the further decomposition of the new products formed. Normally the polarisation first increases on heating, and then decreases as the new products are decomposed. Alkalis have a similar decomposing action, and here in no case was an increase in polarisation observed, very small quantities of alkali being enough to reduce materially the polarisation. Heating of dextrose causes a very small reduction of the reducing power.

Under all pressures lævulose is readily decomposed at somewhat low temperatures. A higher temperature has a greater effect than a longer exposure to a lower temperature. A diminution of the pressure protects the lævulose to some extent. Less concentrated solutions of lævulose are more stable. The products of heating are probably optically inactive and have but a weak reducing power. Lactic and acetic acids protect lævulose from decomposition to some extent. E. F. A.

Yeast-Gum. Hans von Euler and Andor Fodor (*Zeitsch. physiol. Chem.*, 1911, 72, 339—346. Compare Salkowski, Abstr., 1894, i, 222, 316; Meigen and Spring, 1908, ii, 315).—The gum was prepared by Salkowski's method by means of the copper derivative, and in aqueous solution gave $[\alpha]_D^{20}$ $+86{\cdot}95°$. The solution, purified by dialysis, does not give precipitates with phosphomolybdic or phosphotungstic acid. When hydrolysed with dilute sulphuric acid, the ratio mannose : dextrose lies between 40 : 30 and 40 : 40, the mannose being estimated as its phenylhydrazone. J. J. S.

Action of Hydriodic Acid on Starch and Dextrin. William Oechsner de Coninck and A. Raynaud (*Bull. Soc. chim.*, 1911, [iv], 9, 586—587. Compare this vol., i, 423).—The rate of hydrolysis of starch and dextrin by hydriodic acid is proportional to the concentration of the acid. In both cases complete hydrolysis can be effected, and it is reached more quickly with dextrin than with starch. T. A. H.

Electrolytic Decomposition of Cellulose. R. Oertel (*Chem. Zeit.*, 1911, 35, 713).—By the electrolysis of cellulose in a neutral potassium chloride bath the author has succeeded in transforming

it into a product which is soluble in 10% sodium hydroxide, and is probably a new hydroxycellulose. It can be obtained either as retaining the fibrous structure of cellulose, or in such a form that it gives a milky, colloidal solution with water.

Details are reserved for a future communication. T. S. P.

Propylamine Peroxide. EDUARD K. KUROVSKI and L. NISENMAN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 654—655).—In the authors' previous paper, the opinion was expressed that salts of pertitanic acid with organic bases (this vol., i, 183) are really compounds of pertitanic acid and peroxides of amines. They have now been able to prepare propylamine peroxide by the action of propylamine on an ethereal solution of hydrogen peroxide at a low temperature. A heavy, viscous liquid separates, and this, on further cooling, forms a white, crystalline mass. This compound is very unstable and was not completely analysed, but the relation between active oxygen and propylamine indicates that it has the formula $C_3H_7NH_3{\cdot}O_2H$. T. H. P.

Perchlorates of the Choline and Neurine Group. Detection of Choline and Neurine. KARL A. HOFMANN and K. HÖBOLD (*Ber.*, 1911, **44**, 1766—1771).—The fact that quaternary ammonium perchlorates are less soluble in water than the perchlorates of primary, secondary, or tertiary amines (Abstr., 1910, i, 818) has been applied to the detection and isolation of choline and neurine. Choline perchlorate itself is too soluble (100 parts of water dissolve 290 parts of the salt at 15°) for this purpose. *Nitratocholine perchlorate*, $NO_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3{\cdot}ClO_4$, m. p. 185—186° (previously described as choline perchlorate, *loc. cit.*), however, answers admirably. It is obtained by evaporating a 0·2% aqueous solution of choline perchlorate with 2 c.c. of 65% nitric acid on the water-bath, dissolving the residue in a little hot water, and adding a few drops of dilute perchloric acid.

Trimethyldibromoethylammonium perchlorate,

$$CH_2Br{\cdot}CHBr{\cdot}NMe_3{\cdot}ClO_4,$$

large, doubly refracting plates (solubility 2·2 at 15°), and *bromovinyltrimethylammonium perchlorate*, $CH_2{:}CBr{\cdot}NMe_3{\cdot}ClO_4$, elongated plates (solubility 2·65 at 14°), are about half as soluble as neurine perchlorate (*loc. cit.*). C. S.

Molecular State of Organic Ammonium Halides in Non-dissociating Media. ARTHUR HANTZSCH and O. K. HOFMANN (*Ber.*, 1911, **44**, 1776—1783).—Owing to the fact that certain organic ammonium halides have, not only different colours, but also different molecular weights in chloroform (Hantzsch and Leupold, Abstr., 1909, ii, 198), polymerism has been regarded as a cause of difference of colour, and Tinkler has attempted to represent the polymerides of pyridine and acridine methiodides by structural formulæ containing tervalent iodine (Trans., 1909, **95**, 921). Now the authors are of opinion that these supposed polymerides are really only molecular associations, because (i) the molecular weights of organic ammonium halides in the same solvent vary with the nature of the anion in

such a way that the chlorides always have the smallest, the iodides the largest, molecular weights, the bromides and thiocyanates showing intermediate values; (ii) one and the same salt in different, non-dissociating media has a larger or smaller molecular weight according to the greater or smaller associating power of the solvent; (iii) the molecular weight occasionally increases with the concentration in one and the same solvent.

The preceding generalisations have been established by the following experiments. Examined by the ebullioscopic method in dry chloroform, tetrapropylammonium iodide is always quinquemolecular independently of the concentration, tetrapropylammonium chloride is most probably termolecular, whilst triethylammonium chloride is bimolecular and dimethyl- and diethyl-ammonium chlorides are quinquemolecular; the molecular weights of the last three, however, increase with increasing concentration. *iso*Amylammonium chloride does not produce any appreciable rise of the b. p. The degree of association of alkylammonium salts in chloroform does not depend on their molecular weights, but on the amount of the substitution (of the ammonium hydrogen atoms) and the nature of the halogen. The degree of association also depends largely on the solvent; thus, tetra-ethylammonium iodide, which by analogy with tetrapropylammonium iodide should be quinquemolecular in chloroform (actually its solubility is too small for experimental purposes), is almost unimolecular in pyridine.

The molecular weights in chloroform of the 5-phenyl-10-methylacridonium halides given by Hantzsch and Leupold (*loc. cit.*) are too small. The chloride and bromide are bi- to ter-molecular, the thiocyanate is ter- to quadri-molecular, whilst the iodide is constantly quinquemolecular. The simple 5-phenylacridonium halides, however, are only slightly associated in chloroform, whatever the halogen atom. Moreover, 5-phenyl-10-methylacridonium iodide is unimolecular in pyridine or phenol.

A comparison of the preceding results shows that aliphatic and aromatic ammonium halides of the same degree of substitution are about equally strongly associated in the same solvent.

The chloroform used for ebullioscopic measurements must be absolutely free from alcohol or water. A satisfactory quality can be obtained by shaking commercial chloroform with concentrated sulphuric acid for fifteen minutes, washing thoroughly with dilute sodium carbonate and with water, and drying over ignited potassium carbonate; the purified chloroform should be kept in a full bottle over potassium carbonate, in the dark (see further, this vol., i, 673).

C. S.

[Preparation of Quaternary Ammonium Bases.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 231806).—The salts obtained by the exhaustive alkylation of polyacidic bases are converted into quaternary ammonium bases, which are then decomposed by heat.

Hexamethylbutylene-aδ-diammonium iodide,

$$Me_3NI\cdot CH\ \cdot CH_2\cdot CH_2\cdot CH_2\cdot NMe_3I,$$

on treatment with silver oxide yields the corresponding *hydroxide*, a faintly coloured, strongly basic oil, which is decomposed by heat into erythrene (divinyl) and trimethylamine, whilst β-methylbutylene-$\alpha\delta$-diamine yields methyldivinyl (isoprene) when treated in a similar manner. F. M. G. M

Decomposition of Quaternary Ammonium Hydroxides. I. Julius von Braun (*Annalen*, 1911, **382**, 1—49).—The thermal decomposition of quaternary ammonium halides is analogous to that of the trialkylcyanoammonium bromides (compare Abstr., 1910, i, 189). As a rule, the smallest alkyl group is eliminated in the form of alkyl halide, but exceptions are met with when an olefine linking or a phenyl group is present in the alkyl group, and is adjacent to the nitrogen atom. The following are the common alkyl groups arranged in order of decreasing tendency to be eliminated as alkyl halide: allyl, benzyl, methyl, ethyl, propyl, butyl, amyl, phenyl (compare Collie and Schryver, Trans., 1890, **57**, 767; Meyer, this Journ., 1877, ii, 190). Other quaternary ammonium salts, for example, cyanides, thiocyanates, phenoxides, benzoates, and *p*-toluenesulphinates, behave in a similar manner. Experiments made with a number of quaternary ammonium hydroxides show that the behaviour is somewhat different; the order of the groups is: allyl, benzyl, ethyl, propyl, *iso*amyl, hexyl, methyl, *iso*butyl, phenyl (compare Collie and Schryver, *loc. cit.*; Claus and Rautenberg, Abstr., 1881, 584; Claus and Hirzel, 1887, 134; Merling, 1891, 1506). The following numbers give the percentage of the hydroxide transformed into methyl alcohol and dimethylalkylamine: $NMe_3Et{\cdot}OH$, 0%; $NMe_3Pr{\cdot}OH$, 5—10%; $C_4H_9{\cdot}NMe_3{\cdot}OH$, 50%; $C_5H_{11}{\cdot}NMe_3{\cdot}OH$, 60%; $C_6H_{13}{\cdot}NMe_3{\cdot}OH$, 73%; $C_7H_{15}{\cdot}NMe_3{\cdot}OH$, 75%; $C_8H_{17}{\cdot}NMe_3{\cdot}OH$, 75%, and $C_{16}H_{33}{\cdot}NMe_3{\cdot}OH$, 75%, and in each case a decomposition into trimethylamine and an alcohol or olefine also occurs. The following numbers also give the percentage of the hydroxide transformed into methyl alcohol and mixed tertiary base:

$OPh{\cdot}[CH_2]_3{\cdot}NMe_3{\cdot}OH$, 10%; $OPh{\cdot}[CH_2]_4{\cdot}NMe_3{\cdot}OH$, 55%;
$OMe{\cdot}[CH_2]_5{\cdot}NMe_3{\cdot}OH$, 60%; $OPh{\cdot}[CH_2]_5{\cdot}NMe_3{\cdot}OH$, 60%;
$NH_2{\cdot}[CH_2]_5{\cdot}NMe_3{\cdot}OH$, 60%; $COPh{\cdot}NH{\cdot}[CH_2]_5{\cdot}NMe_3{\cdot}OH$, 60%.

The amount of olefine tends to diminish, and the amount of corresponding alcohol to increase, with an increase of the molecular weight of the alkyl group present in the trimethylalkylammonium hydroxide, so that trimethylcetylammonium hydroxide yields practically no cetene. The formation of an olefine or unsaturated compound is regarded as a primary decomposition, and is not attributed to a secondary decomposition of an alcohol. The following numbers are also given:

$CH_2Ph{\cdot}NMe_3{\cdot}OH$, little; $CH_2Ph{\cdot}CH_2{\cdot}NMe_3{\cdot}OH$, 0%;
$CH_2Ph{\cdot}[CH_2]_2{\cdot}NMe_3{\cdot}OH$, 70%; $CH_2Ph{\cdot}[CH_2]_4{\cdot}NMe_3{\cdot}OH$, 75%,

where the number indicates the percentage of the hydroxide decomposed into methyl alcohol and mixed tertiary amine. The general conclusion drawn is, that the manner in which a quaternary ammonium hydroxide decomposes depends first on the tendency of the mobile light groups to be eliminated as alcohols, and, secondly, on the tendency by means of the elimination of water to form olefines of symmetrical

structure. The influence of the second factor is seen by a comparison of the products of decomposition of *n*-heptyl- and *n*-octyl-trimethylammonium hydroxide with the corresponding *cyclo*heptyl and *cyclo*octyl hydroxides (compare Willstätter, Abstr., 1901, i, 223; Willstätter and Waser, 1910, i, 366). Hexenyltrimethylammonium hydroxide (Merling) gives 80% of trimethylamine, owing to the fact that a symmetrical diolefine, $CH_2\dot{:}CH\cdot CH_2\cdot CH_2\cdot CH\dot{:}CH_2$, can be formed.

As quaternary ammonium hydroxides are readily prepared, the manner in which they decompose on heating is of importance in connection with the preparation of mixed tertiary amines. The simplest method of preparing butyl-, amyl-, hexyl-, heptyl-, octyl-, and cetyl-dimethylamines and similar compounds is probably by decomposing the corresponding alkyltrimethylammonium hydroxides.

The quaternary ammonium salts can be prepared by the complete methylation of the primary amine, or, in some cases, by the union of trimethylamine with the necessary alkyl iodide or bromide. As a rule, the quaternary hydroxides can be distilled under atmospheric pressure, and the basic products separated from the neutral compounds by means of dilute acid.

Trimethyl-n-*butylammonium iodide*, $C_7H_{18}NI$, can be separated from potassium iodide as it dissolves in warm chloroform; it softens at 225°, and has m. p. 230° (decomp.). The corresponding hydroxide is syrupy, and when heated yields dimethylbutylamine, $NMe_2\cdot C_4H_9$, as a mobile oil, b. p. 96°, sparingly soluble in water. The *platinichloride*,

$$2C_6H_{15}N,H_2PtCl_6,$$

crystallises in brilliant, reddish-yellow plates, m. p. 110°, and the *picrate* separates from alcohol in similar plates, m. p. 98°.

Trimethylamylammonium iodide has m. p. 215° (Willstätter and Waser give 222°), and when decomposed gives Δ^a-amylene, but no amyl alcohol. a-Dimethylaminopentane yields a *picrate*,

$$C_7H_{17}N,C_6H_3O_7N_3,$$

which crystallises from alcohol in brilliant, long needles, m. p. 100°. Cyanogen bromide reacts with an ethereal solution of the tertiary base, yielding trimethylamylammonium bromide and *methyl*-n-*amylcyanamide*, $C_5H_{11}\cdot NMe\cdot CN$. The latter is an oil with a fragrant odour, has b. p. 109°, and when boiled with 30% aqueous alcoholic sulphuric acid yields methyl-*n*-amylamine (Löffler, Abstr., 1910, i, 632; the picrate has m. p. 121°, not 119—120°).

Trimethylhexylammonium iodide, $C_6H_{13}\cdot NMe_3I$, prepared from *n*-amylamine (Braun and Sobecki, this vol., i, 128), has m. p. 167°; the corresponding *hydroxide* is a solid, and when distilled yields Δ^a-hexylene, b. p. 62—63°/740 mm. and D_{20}^{20} 0·6686. *Dimethyl*-n-*hexylamine*, $C_6H_{13}\cdot NMe_2$, has b. p. 147°; the *platinichloride* is readily soluble in water and has m. p. 126—127°, and the *picrate* has m. p. 101°.

Trimethyl-n-*heptylammonium iodide*, $C_{10}H_{24}NI$, forms crystalline plates, which soften at 143° and melt at 145°. The *hydroxide* is a solid, and when distilled yields Δ^a-heptylene, heptyl alcohol, and *dimethyl*-n-*heptylamine*, $C_9H_{21}N$. The tertiary base has b. p. 172°, yields a *platinichloride* in the form of felted, reddish-yellow needles, m. p. 139°, and a *picrate*, m. p. 83°. When treated with cyanogen bromide the tertiary base yields *methylheptylcyanamide*, $C_7H_{15}\cdot NMe\cdot CN$, as a

colourless oil with b. p. 142°/15 mm., and this on hydrolysis with 33% sulphuric acid gives the secondary base, *methylheptylamine*, $C_8H_{19}N$, with b. p. 168°. The *picrate* crystallises in yellow needles, m. p. 97°, and the *platinichloride* in orange plates, m. p. 168°. The *carbamide*, $C_7H_{15}\cdot NMe\cdot CO\cdot NH_2$, crystallises from a mixture of ether and light petroleum in colourless, glistening plates, m. p. 100°.

Trimethyl-*n*-octylammonium iodide, prepared from trimethylamine and *n*-octyl iodide, has m. p. 138° (Mugdan, Abstr., 1898, i, 157, gives 139—141°); the *hydroxide* is a solid, and yields a mixture of octylene and octyl alcohol, together with *dimethyl*-n-*octylamine*, $C_8H_{17}\cdot NMe_2$, b. p. 194°. The *platinichloride* of the tertiary base forms long needles, m. p. 120°, and the *picrate* has m. p. 62—65°.

Trimethylcetylammonium iodide, $C_{19}H_{42}NI$, crystallises in felted needles, m. p. 222°, and on treatment with moist silver oxide shows a great tendency to form colloidal silver iodide, and this complicates the preparation of the quaternary hydroxide. The hydroxide when heated does not melt, and yields *dimethylcetylamine*, $C_{16}H_{33}\cdot NMe_2$, with b. p. 193—205°/18 mm. The base contains small amounts of non-nitrogenous products, and is best purified by means of the *picrate*, $C_{18}H_{39}N,C_6H_3O_7N_3$, which crystallises in long needles, m. p. 69°. The pure base has b. p. 203—205°/17 mm., and its *platinichloride* has m. p. 83°, and is practically insoluble in hot water. Cetyl alcohol is also formed during the decomposition of the hydroxide.

γ-Phenoxypropyltrimethylammonium iodide, $OPh\cdot[CH_2]_3\cdot NMe_3I$, is best prepared from trimethylamine and γ-phenoxypropyl iodide, and crystallises from alcohol in glistening plates, m. p. 174°. The hydroxide on distillation yields trimethylamine and phenyl allyl ether, together with a small amount of phenyl γ-dimethylaminopropyl ether (compare Knorr and Roth, Abstr., 1906 ,i, 457). *δ-Phenoxybutyltrimethylammonium iodide*, $C_{13}H_{22}ONI$, is sparingly soluble, and has m. p. 169°. When distilled the *hydroxide* yields *phenyl Δ^a-butenyl ether*,

$$CH_2{:}CH\cdot CH_2\cdot CH_2\cdot OPh,$$

b. p. 208—210°, together with *phenyl δ-dimethylaminobutyl ether*, $OPh\cdot[CH_2]_4\cdot NMe_2$, with b. p. 139—140°/13 mm. The *platinichloride* is oily, and the *picrate* has m. p. 108°.

ε-Phenoxyamyltrimethylammonium iodide, $OPh\cdot[CH_2]_5\cdot NMe_3I$, has m. p. 185°, and its oily *hydroxide* when distilled yields phenyl amylenyl ether (Braun and Trümpler, Abstr., 1910, i, 26) and *phenyl ε-dimethylaminoamyl ether*, $OPh\cdot[CH_2]_5\cdot NMe_2$. The latter is a colourless oil with b. p. 149°/11 mm., and yields a *picrate*, m. p. 99°.

Methyl ε-benzoylaminoamyl ether and phosphorus pentachloride yield benzonitrile and methyl ε-chloroamyl ether, together with αε-dichloropentane. When a mixture of the two latter compounds is boiled with an alcoholic solution of potassium iodide a mixture of the corresponding iodo-compounds is obtained, and these with trimethylamine yield *hexamethylamylenediammonium iodide*,

$$NMe_3I\cdot[CH_2]_5\cdot NMe_3I,$$

and a small amount of *ε-methoxyamyltrimethylammonium iodide*, $OMe\cdot[CH_2]_5\cdot NMe_3I$. The former is sparingly soluble in alcohol, turns brown at 200°, and decomposes between 268° and 273°. The latter dissolves readily in alcohol, and has m. p. 123—124°. When

the hydroxide corresponding with the methoxy-salt is distilled, the products are methyl amylenyl ether and *methyl ε-dimethylaminoamyl ether*, $OMe\cdot[CH_2]_5\cdot NMe_2$.

ε-Benzoylaminoamyltrimethylammonium hydroxide (Abstr., 1910, i, 820) has to be decomposed under reduced pressure, and gives a 60% yield of benzoyldimethylamylenediamine and a 40% yield of pentenylbenzamide.

The *hydrochloride* of *aminoamyltrimethylammonium chloride*,

$$HCl,NH\cdot[CH_2]_5\cdot NMe_3Cl,$$

obtained by hydrolysing the corresponding benzoyl derivative with concentrated hydrochloric acid at 160°, forms hygroscopic crystals, and the *platinichloride* forms red crystals, m. p. 218°. To obtain the hydroxide, the chloride is transformed into the sulphate by means of silver sulphate, and this is then decomposed with barium hydroxide solution. *Aminoamyltrimethylammonium hydroxide* is a sticky mass, and when distilled under atmospheric pressure yields *as*-dimethylcadaverine and methyl alcohol, together with trimethylamine, water, and Δ^{a}-*pentenylamine*. The unsaturated amine is a colourless oil with an intense odour, has b. p. 91—94°, absorbs water and carbon dioxide, and yields a *platinichloride*, $C_{10}H_{24}N_2PtCl_6$, in the form of red plates, m. p. 166° (decomp.). The *aurichloride* sinters at 180° and has m. p. 195°, and the *benzenesulphonyl* derivative is oily and readily soluble in alkalis. The quaternary salt, *trimethylpentenylammonium iodide*, $C_5H_9NMe_3I$, has m. p. 195°.

β-Phenylethyltrimethylammonium bromide (this vol., i, 35) is readily prepared from β-phenylethyl bromide and trimethylamine, and the corresponding hydroxide decomposes into trimethylamine and styrene when its aqueous solution is heated on the water-bath (compare Freund, Abstr., 1899, i, 308; Pschorr, 1904, i, 767; 1905, i, 590).

γ-Phenylpropyltrimethylammonium hydroxide (compare Tafel and Senfter, Abstr., 1894, i, 579) is more stable, and is decomposed when strongly heated, giving a 70% yield of phenylpropyldimethylamine, b. p. 225°, and a 28% yield of propenylbenzene, b. p. 169—171°.

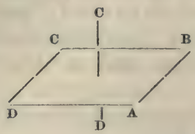
ε-Phenylamyltrimethylammonium hydroxide (Abstr., 1910, i, 844) gives a 75% yield of *ε-phenylamyldimethylamine*, $CH_2Ph\cdot[CH_2]_4\cdot NMe_2$, as a colourless liquid with b. p. 134—135°; its *picrate* and platinichloride are both oily. A 20% yield of *phenylamylene*,

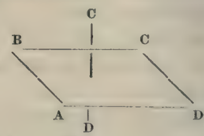
$$CH_2Ph\cdot CH_2\cdot CH_2\cdot CH{:}CH_2\ (?),$$

is also formed. It is a colourless liquid with b. p. 197—198°, D_4^{20} 0·8851, and n_D 1·5064. The position of the olefine linking has not been settled. J. J. S.

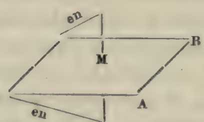
The Asymmetric Cobalt Atom. I. ALFRED WERNER [with V. L. KING and E. SCHOLZE] (*Ber.*, 1911, 44, 1887—1898).—According to the author's co-ordination theory, compounds containing the following complex radicles should give optical isomerides: (1) $\left[{}^{B}_{C}M^{A_3}_{D}\right]$, when B, C, and D occupy the corners of one of the faces of

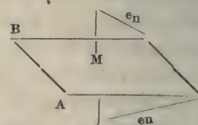
an octahedron. (2) $\left[{}^{A}_{B}M^{C_2}_{D_2}\right]$, when the groups combined with the metal atom, M, take up the following positions:





In the second case it is not necessary for the groups C and D to be different, and one of the simplest cases would be when the groups CC and DD are replaced by ethylenediamine, giving compounds of the type $\left[{}^{A}_{B}M\ en_2\right]$. When the groups A and B are in the *cis*-position, the two optical isomerides would be represented by the space formulæ:





The compounds 1-chloro-2-amminediethylenediaminecobalt salts, $\left[{}^{Cl}_{H_3N}Co\ en_2\right]X_2$, and 1-bromo-2-ammine-diethylenediaminecobalt salts, $\left[{}^{Br}_{H_3N}Co\ en_2\right]X_2$, have been prepared and resolved into their optically-active isomerides by means of *d*-bromocamphorsulphonic acid. The salts of the bromo-ammine series are the more easily resolved, because of the great difference in solubility between the isomeric *d*-bromocamphorsulphonates. In both series the *d*-bromocamphorsulphonate of the *d*-isomeride is the more sparingly soluble.

The active compounds are very stable. The aqueous solutions of the bromides of the bromo-ammine series can be kept for a long time at the ordinary temperature, or even heated just to boiling without undergoing racemisation. The activity is also maintained when the bromine atom in the complex is taken out with silver nitrate, according to the equation:

$$\left[{}^{Br}_{H_3N}Co\ en_2\right]Br_2 + 3AgNO_3 + H_2O = \left[{}^{H_2O}_{H_3N}Co\ en_2\right](NO_3)_3 + 3AgBr,$$

showing that the aquo-amminediethylenediaminecobalti-salts also give optical isomerides. No racemisation takes place when various salts are formed in the two series, as will be seen in the experimental part.

The fact that such active compounds have been prepared shows that the distinction between valency compounds and molecular compounds can be maintained no longer.

Optically-active Chloro-amminediethylenediaminecobalti-salts, YX_2, where $Y = \left[{}^{Cl}_{H_3N}Co\ en_2\right]$.—The starting point for the preparation of these salts was the racemic compound 1-chloro-2-amminediethylenediaminecobalti-chloride, $\left[{}^{(1)\ Cl}_{(2)\ H_3N}Co\ en_2\right]Cl_2$, which was prepared by

triturating acid-free 1 : 6-dichlorodiethylenediaminecobalti-chloride with concentrated ammonia. The green salt first dissolves and then the solution sets to a mass of red crystals of the required salt. Forty grams of this salt were dissolved in 250 c.c. of water, and a solution of 115 grams of silver *d*-bromocamphorsulphonate in 350 c.c. of water added. After collecting the silver bromide, the filtrate, on keeping, deposits short, slender, red prisms. These are collected as soon as felted, silky needles begin to form alongside them, and the filtrate, after four to six hours, solidifies to a mass of these needles. The former compound consists of d-1-*chloro-2-amminediethylenediamine-cobalti*-d-*bromocamphorsulphonate*, $Y(O_3S\cdot O\cdot C_{10}H_{14}Br)_2$, and after recrystallisation from water forms flat, slender, prismatic crystals; $[\alpha]_C = +69\cdot5°$ and $[M]_C = +592\cdot14°$. The latter compound is l-1-*chloro-2-amminediethylenediaminecobalti*-d-*bromocamphorsulphonate*, and forms bluish-red, long, slender needles, with $[\alpha]_C = +31\cdot25°$ and $[M]_C = +362\cdot1°$. The d-*bromide*, YBr_2, was prepared from the bromocamphorsulphonate either by direct treatment with concentrated hydrobromic acid, or else by forming the sparingly soluble *dithionate*, and triturating that compound with concentrated hydrobromic acid. It forms cherry-red, small, leaf-like crystals, which have $[\alpha]_C = +43\cdot1°$ and $[M]_C = +172\cdot34°$. The rotatory power was unchanged when the bromide was again obtained after being transformed successively into the dithionate, bromide, platinichloride, nitrate and bromide, neither did heating the solution to 70° alter the rotation. The l-*bromide* was obtained in the same way as the d-*bromide*, and corresponded completely with the latter in colour, shape of crystals, and solubility; $[\alpha]_C = -43\cdot1°$ and $[M]_C = -168\cdot43°$.

Optically-active 1-*bromo*-2-*amminediethylenediaminecobalti-salts*, YX_2, where $Y = \left[{}^{Br}_{H_3N}Co\,en_2\right]$, were prepared from 1:2-bromoammine-diethylenediaminecobalti-bromide, $\left[{}^{(1)\ Br}_{(2)\ H_3N}Co\,en_2\right]Br_2$. This salt was obtained according to the following two methods: (1) 1 : 6-Dibromodiethylenediaminecobalti-bromide is moistened with water and treated with 1 : 1 ammonia at a low temperature until the green salt is completely transformed into reddish-violet:

$$\left[{}^{(1)\ Br}_{(6)\ Br}Co\,en_2\right]Br + NH_3 = \left[{}^{(1)\ Br}_{(2)\ H_3N}Co\,en_2\right]Br_2.$$

(2) Ten grams of tetraethylenediaminediaquotetroldicobalticobaltosulphate and 30 grams of ammonium bromide are covered with water and the mixture heated. A reddish-violet solution results, which on cooling and saturating with sodium bromide deposits the required salt:

$$\left[en_2\,Co{}^{\cdot OH\cdot}_{\cdot OH\cdot}Co(OH_2)_2{}^{\cdot OH\cdot}_{\cdot OH\cdot}Co\,en_2\right](SO_4)_2 + 6NH_4Br + 2H_2O =$$

$$[Co(OH_2)_6]SO_4 + 2\left[{}^{Br}_{H_3N}Co\,en_2\right]Br_2 + (NH_4)_2SO_4 + 2NH_3.$$

The resolution of this salt by means of the *d*-bromocamphorsulphonate was carried out in a manner similar to that described for the chloroammine salt. The d-1-*bromo-2-amminediethylenediaminecobalti*-d-*bromocamphorsulphonate*, $Y(O_3S\cdot O\cdot C_{10}H_{14}Br)_2$, crystallises out first in the form of dark, thick, long, reddish-violet needles; $[\alpha]_C = +65\cdot7°$ and

$[M]_C = +588 \cdot 7°$. The addition of sodium dithionate to the mother liquors gives a precipitate of a racemic dithionate; this is collected, and further addition of sodium dithionate to the filtrate produces, on standing, a deposit of the active *dithionate*, which serves as the starting point for salts of the *l*-series.

The d-*chloride*, YCl_2, was obtained from the *d*-bromocamphorsulphonate by treatment with concentrated hydrochloric acid. It forms dark reddish-violet, shining, flat crystals, and has $[\alpha]_C = +50 \cdot 6°$ and $[M]_C = +175 \cdot 6°$. The solution shows no signs of racemisation after keeping for six days. The d-*bromide*, YBr_2, was obtained similarly, using hydrobromic acid, and forms small, shining, dark violet needles; $[\alpha]_C = +46 \cdot 25°$ and $[M]_C = +201 \cdot 65°$. The 0·8% aqueous solution was not racemised when heated for a short time at the boiling point. The d-*nitrate*, $Y(NO_3)_2,H_2O$, prepared from the bromocamphorsulphonate and fuming nitric acid, forms dark violet columns. It loses $1H_2O$ at 100°, and has $[\alpha]_C = +45 \cdot 0°$ and $[M]_C = +188°$.

The l-*bromide*, YBr_2, was obtained as dark reddish-violet, needle-shaped crystals by treating the *l*-dithionate with concentrated hydrobromic acid. It has $[\alpha]_C = -45°$ and $[M]_C = -196 \cdot 2°$. T. S. P.

Oxidation of the Amino-acids. I. Glycine and Cystine. W. Denis (*J. Biol. Chem.*, 1911, 9, 365—374).—Glycine on complete oxidation with alkaline potassium permanganate yielded oxalic acid, carbon dioxide, ammonia, and nitric acid. If the oxidation was incomplete, traces of formic and glyoxylic acids could be detected. A modification of the existing methods for the preparation of cystine is described; on complete oxidation it yields sulphuric, oxalic, acetic, and nitric acids, carbon dioxide, ammonia, and free sulphur; if the oxidation was incomplete, traces of pyruvic acid were found.

W. D. H.

Action of *iso*Butylamine and Di-*iso*butylamine on α-Bromobutyric Acid. Jean Nivière (*Compt. rend.*, 1911, 152, 1673—1674).—α-Hydroxybutyric acid is the only product when di-*iso*butylamine acts on α-bromobutyric acid. *iso*Butylamine reacts, forming iso*butylamine* α-iso*butylaminobutyrate*. α-iso*Butylaminobutyric acid*, $C_4H_9 \cdot NH \cdot CHEt \cdot CO_2H$, occurs in pearly lamellæ, which sublime and decompose without melting. Heated in hydrogen chloride at 180—200° it does not form a piperazine derivative, but loses carbon dioxide, yielding the corresponding secondary amine. The amino-acid forms a *hydrochloride*, crystallising with $1 \cdot 5H_2O$, a *platinichloride* crystallising in red needles with $2H_2O$, decomp. 100—110°, an *aurichloride*, a *picrate*, and *copper* and *silver* salts. The *hydrochloride*, *platinichloride*, and *picrate* of the *ethyl* ester are uncrystallisable. W. O. W.

Action of Oxalyl Chloride on Amines and Amides. J. Th. Bornwater (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 42—46).—Oxalyl chloride in ethereal solution at the ordinary temperature gives with piperidine, oxalylpiperidide; with aniline, oxanilide, and with *o*- and *m*-nitranilines, the corresponding dianilides. With 2 : 4-dinitroaniline in boiling benzene, oxalyldi-2 : 4-dinitroanilide resulted.

Oxalyl chloride reacts *directly* in boiling benzene with the hydrochlorides of the amines, such as aniline and piperidine, also with those of the amino-acid esters. Of the latter, the following compounds have been prepared:

Oxalyldiglycine ethyl ester, $C_2O_2(NH\cdot CH_2\cdot CO_2Et)_2$, m. p. 143°.

Oxalyldiglycylglycine ethyl ester,

$$C_2O_2(NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et)_2,$$

lustrous leaflets, giving the biuret reaction, m. p. 250°.

Oxalyldi-diglycylglycine ethyl ester,

$$C_2O_2(NH\cdot CH_2\cdot[CO\cdot NH\cdot CH_2]_2\cdot CO_2Et_2,$$

forming silky needles, giving a reddish-violet biuret reaction, m. p. 302°.

As an example of the amino-derivatives of dibasic acids, the hydrochloride of the diethyl ester of glutamic acid was found to give *oxalyldi-glutaminic diethyl* ester,

$$C_2O_2[NH\cdot CH(CO_2Et)\cdot CH_2\cdot CH_2\cdot CO_2Et]_2,$$

m. p. 94·5°.

The author suggests the possibility of obtaining similar oxalyl compounds from polypeptides in general, and of the ultimate synthesis of the proteins, which, as shown by Schützenberger many years ago, all yield oxalic acid by resolution with barium hydroxide.

With simple amides, oxalyl chloride yields in some cases carbonyl and not oxalyl derivatives. For example, with benzamide, di-benzoylcarbamide, and with chloroacetamide, *dichloroacetylcarbamide*,

$$CO(NH\cdot CO\cdot CH_2Cl)_2,$$

white needles, m. p. 171°, is produced, but benzanilide gives *oxalyl di-benzanilide*, $C_2O_2(NPh\cdot COPh)_2$, m. p. 210°.

Ethyl urethane yields carbonyl diethylurethane, but methylethyl urethane gives *oxalyldimethylethylurethane*, $C_2O_2(NMe\cdot CO_2Et)_2$, m. p. 67°. Carbamide gives, in ether at the ordinary temperature, parabanic acid and, apparently *oxalyldiureide*, $C_2O_2(NH\cdot CO\cdot NH_2)_2$, which is quite different from Grimaux's compound (Abstr., 1880, 105) wrongly termed oxalyldiureide in German literature. It is quite insoluble in the ordinary solvents, and gives no biuret reaction.

s-Dimethylcarbamide gives cholestrophan, but *as*-dimethylcarbamide (in boiling benzene) gives *carbonyldi*-as-*dimethylcarbamide*,

$$CO<\begin{matrix}NH\cdot CO\cdot NMe_2\\NH\cdot CO\cdot NMe_2\end{matrix},\tfrac{1}{2}H_2O,$$

in beautiful prisms, m. p. 140°. J. D. K.

Iodogorgonic Acid. MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1911, **72**, 505—506).—Polemical. A point of priority, Wheeler and Jamieson having claimed that they and not the author were the first to describe di-iodotyrosine as a decomposition product of iodogorgonic acid. W. D. H.

Reduction of Potassium Cyanate with Hydrogen. A. P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 650—651).—When dry hydrogen is passed through a tube heated at 400° in an electric furnace and containing a platinum boat filled with potassium cyanate, the latter undergoes reduction to the cyanide. The reaction is

apparently complicated by secondary reactions, since the loss in weight of the cyanate often exceeds the increase in weight of a calcium chloride tube situate at the far end of the tube. T. H. P.

Formation of Cyanates from Nitrites. A. P. Lidoff (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 651—652).—If a mixture of sodium nitrite (5 grams) with 3—5 times the calculated quantity of finely divided carbon (5 grams) is introduced, in small portions, into a heated platinum dish or crucible, energetic reduction of the nitrite occurs, an aqueous solution of the fused mass no longer developing nitric oxide when shaken with mercury and sulphuric acid. The products formed are cyanate, a small proportion of cyanide and sodium carbonate, together with other cyanogen compounds of an acid character. One of the latter forms a barium salt which is soluble in a neutral solution, but is immediately deposited in shining scales on addition of a small quantity of potassium hydroxide; when freshly prepared, this salt does not give any evolution of gas when treated with acid, but it darkens later and then yields with acids, "carbon acid" gas, the weight of which is rather less than that of carbon dioxide.

T. H. P.

Oxidation of Sodium Cyanamide and Cyanates with Hydrogen Peroxide and Alkaline Bromine Solution. A. P. Lidoff (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 652—653).—By the interaction of sodium cyanamide solution and a solution of bromine in sodium hydroxide, free from carbon dioxide, in a nitrometer, only about 15—25% of the nitrogen is evolved. Decomposition of the alkaline solution with phosphoric acid results in the development of "carbon acid" gas with a small admixture of hydrogen bromide.

A 5% solution of sodium cyanamide was oxidised by hydrogen peroxide, the latter being added first in the cold and finally on boiling until the solution, which originally gave a yellow precipitate of lead cyanamide with lead acetate, gave a pure white precipitate. On boiling the liquid, a distinct smell of ammonia was observed. To the cooled liquid, lead acetate was added as long as a precipitate was formed, this being then washed with water, alcohol and ether. The lead salt weighed 12 grams, and the gas evolved with potassium hydroxide, 1·902 grams.

When potassium cyanate and an alkaline solution of bromine are allowed to react and barium chloride is added to the liquid, a precipitate is obtained which, with phosphoric acid, gives a quantity of "carbon acid" gas, 1·872—1·915, corresponding closely with that obtained from the cyanamide; similar results are obtained when the oxidation is effected by hydrogen peroxide.

The conclusion is drawn that, under the above conditions, the cyanogen group undergoes oxidation to oxycyanogen, CNO.

T. H. P.

Constitution of Prussian Blue. Arnaldo Brioni (*Boll. Chim. Farm.*, 1911, **50**, 165—169).—Polemical. The author furnishes arguments and experimental evidence against the view put forward by

Tarugi and Revello (*Atti VI Congr. Chim. appl.*, 1906) that Prussian blue is to be regarded as a ferrous or ferrous potassium salt of an oxyferrohydrocyanic acid. R. V. S.

Cobaltinitrites. ARTHUR ROSENHEIM and ABRAHAM GARFUNKEL (*Ber.*, 1911, **44**, 1865—1873).—The authors show that the complex cobaltinitrites previously investigated by Rosenheim and Koppel (Abstr., 1898, ii, 430), and salts of a cobalt-3-hydroxo-3-nitrite anion studied by Hofmann and Buchner (Abstr., 1909, i, 775) belong to the same class. Two cobalt-3-guanidinium-3-hydroxo-3-nitrites have also been obtained, these probably being isomerides, as predicted by Werner's theory, and the first of their kind. Furthermore, a new class of compounds, the cobalt-2-acetylacetonato-2-nitrites, has been prepared.

Cobalt-3-hydroxo-3-nitrites.—When a concentrated solution of cobalt-3-sodium-6-nitrite, $Na_3Co(NO_2)_6$, to which an equimolecular proportion of guanidine carbonate has been added, is evaporated over sulphuric acid, amber-coloured, tabular crystals are obtained, having the composition $(CN_3H_6)_2Na[Co(NO_2)_6]$, which show all the reactions of the cobalt-6-nitrites. When 3 mols. of guanidine carbonate are used to 1 mol. of the cobaltinitrite, a deep red solution results, from which garnet-red, shining crystals, having the composition $(CN_3H_6)_3[Co(OH)_3(NO_2)_3]$, are obtained. They agree, in all their properties, with the crystals described by Hofmann and Buchner as having the composition $(CN_3H_6)_2Na[Co(OH)_3(NO_2)_3]$, but do not contain sodium.

The mother liquors from the garnet-red crystals give a further deposit of dark brick-red needles, having the formula

$$(CN_3H_6)_3[Co(OH)_3(NO_2)_3],$$

and agreeing in properties and composition with the compound previously obtained by Hofmann and Buchner.

The two compounds of the same composition (garnet-red crystals = A; brick-red = B) differ in appearance, solubility, and some precipitation reactions. With a solution of thallous nitrate, A gives immediately a microcrystalline, cinnabar-red precipitate, having the composition $Tl_2H[Co(OH)_3(NO_2)_3]$, whereas B, after a few minutes, deposits brownish-red crystals of the formula $Tl_2(CN_3H_6)[Co(OH)_3(NO_2)_3]$.

The *zinc* salt, previously prepared by Rosenheim and Koppel (*loc. cit.*), is now found to have the formula

$$ZnH[Co(OH)_3(NO_2)_3],4H_2O;$$

with thallous nitrate the solution deposits the above-mentioned cinnabar-red thallium salt, proving that the zinc salt belongs to the cobalt-3-hydroxo-3-nitrites. The *silver* salt has the formula

$$Ag_2H[Co(OH)_3(NO_2)_3].$$

Cobalt-2-hydroxo-4-nitrites.—The strontium salt,

$$SrH[Co(OH)_2(NO_2)_4],4H_2O,$$

is the only one which has been obtained pure. It is prepared by leading nitrous gases into a cooled suspension of cobalt carbonate and strontium carbonate, and forms small, garnet-red prisms, which are unstable as such, and in solution, nitrous acid being liberated.

Cobalt-2-acetylacetonato-2-nitrites.—When concentrated solutions of

sodium acetylacetonate and sodium cobaltinitrite are mixed and kept, purple-red crystals are deposited, having the composition

$$Na[Co(C_5H_7O_2)_2(NO_2)_2],5H_2O,$$

which lose $5H_2O$ in a vacuum over sulphuric acid. The anhydrous salt is also obtained as slender, bright-red needles, when the solution crystallises at 30°. The aqueous solution gives characteristic precipitates with salts of the alkali metals, of thallium and of silver. The *potassium* salt, $K[Co(C_5H_7O_2)_2(NO_2)_2],H_2O$, forms hair-like, light brownish-red needles; the *ammonium*, *caesium*, and *rubidium* salts are similar in appearance to the potassium salt. The *thallium* salt, $Tl[Co(C_5H_7O_2)_2(NO_2)_2]$, forms a microcrystalline, brownish-yellow precipitate. Dilute solutions of the sodium salt give, with silver nitrate, reddish-brown, shining needles of the composition

$$Ag[Co(C_5H_7O_2)_2(NO_2)_2],$$

whereas a saturated solution gives a dark yellow precipitate of the composition $Ag_2[Co(C_5H_7O_2)_2(NO_2)_3]$.

A solution of the sodium salt, on being boiled, deposits deep green crystals, together with brown, flocculent decomposition products. The crystals are soluble in ether, and consist of cobaltiacetylacetonate, $Co(C_5H_7O_2)_3$. When sodium acetylacetonate is added to the mother liquors from which the salt $Na[Co(C_5H_7O_2)_2(NO_2)_2]$ has crystallised, bright red, hair-like needles having the composition $Na[Co(C_5H_7O_2)_3]$ are obtained. This compound gives the colour reaction of acetylacetone with ferric chloride, whereas the complex cobalt-2-acetylacetonato-2-nitrites do not.

Other 1 : 3-diketones, such as benzoylacetone, as also acetoacetic ester, give compounds analogous to those obtained with acetylacetone.

Zinc and *cadmium acetylacetonates*, $Zn(C_5H_7O_2)_2$ and $Cd(C_5H_7O_2)_2$, were obtained as white needles by the action of sodium acetylacetonate on zinc and cadmium sulphates respectively. T. S. P.

Synthesis of Pentamethylenediguanidine. OTTO RIPKE (*Zeitsch. physiol. Chem.*, 1911, **72**, 484—485).—When an aqueous solution of pentamethylenediamine is left in contact with a large excess of cyanamide for seventeen days in a desiccator at the ordinary temperature, the solution then treated with sulphuric acid and silver sulphate, then neutralised with barium hydroxide and filtered, and the filtrate saturated with barium hydroxide, a precipitate is obtained, which, after treatment with sulphuric acid and hydrogen sulphide, yields pentamethylenediguanidine sulphate. This forms well developed crystals, sparingly soluble in water, and is not molten at 300°.

The *aurichloride*, $C_7H_{18}N_6,2HAuCl_4$, crystallises well, and has m. p. 161°. The structural formula suggested for the base is

$$CH_2[CH_2\cdot CH_2\cdot NH\cdot C(NH_2)\colon NH]_2.$$

The reaction between cyanamide and pentamethylenediamine is quite different from that between cyanamide and tetramethylenediamine (Kossel, Abstr., 1910, i, 655). J. J. S.

Relations between Certain Derivatives of Oxygen and of Nitrogen. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 625—627. Compare Abstr., 1910, ii, 844, 948).—Harries (Abstr.,

1910, i, 607) has shown that the action of ozone on an oxime results in the formation of an ozonide, which has a ring structure, and which can be resolved into a ketone and nitric acid. The latter contains the grouping O·N(OH)·O in place of the O·O·O grouping of the ozone. Nitric acid can further be transformed into the amino-compound, $O{\cdot}N(NH_2){\cdot}O$, which readily loses a molecule of water, giving nitrous oxide, N·N·O, two of the oxygen atoms of ozone now having been replaced by nitrogen atoms. Then, by the action of ammonia in the form of its sodium derivative, nitrous oxide is converted into hydrazoic acid, the total change from ozone being: $\begin{matrix}O\\|\\O\end{matrix}\!>\!O \longrightarrow \begin{matrix}N\\||\\N\end{matrix}\!>\!NH$. These two extreme terms of this series of changes exhibit considerable similarity. Thus, they are both formed with absorption of heat and are explosive, and both are poisonous and have suffocating odours. Both react with compounds having multiple linkings, ozone forming ozonides and hydrazoic acid the analogous triazoles:

$$CH\vdots CH + N_3H = N\lessdot\begin{matrix}NH{\cdot}CH\\ \quad\;\;||\\N—CH\end{matrix}.$$

T. H. P.

Hydroaromatic Compounds. Hydrocarbon, C_9H_{12}, of the Semibenzene Series. KARL AUWERS and KARL MÜLLER (*Ber.*, 1911, 44, 1595—1608).—The previously described semibenzene derivatives all contain chlorine, whilst hydroaromatic ketones unite with hydrogen and form phenols with the elimination of methylene chloride when attempts are made to prepare semibenzene derivatives from them. The alcohols obtained from these ketones by the Grignard reaction behave differently.

The alcohol, $OH{\cdot}CMe\!<\!\begin{matrix}CH\vdots CH\\CH\vdots CH\end{matrix}\!>\!CMe{\cdot}CHCl_2$, is converted on treatment with sodium and moist ether into 1:1:4-*trimethyl*cyclo-$\Delta^{2,5}$-*hexadiene*-4-*ol*, although the yield is unsatisfactory, and this is readily converted into 1:1-*dimethyl*-4-*methylene*cyclo-$\Delta^{2,5}$-*hexadiene*,

$$CH_2\vdots C\!<\!\begin{matrix}CH\vdots CH\\CH\vdots CH\end{matrix}\!>\!CMe_2.$$

The alcohol, *trimethyl*cyclo*hexadienol*, crystallises in colourless, lustrous needles, m. p. 43—44°, b. p. 169—170°/760 mm., and is characterised by the fact that when pure it distils without decomposition. On the other hand, it is very sensitive to acids, and even pure preparations decompose slowly on keeping. Strong and weak acids and acid salts all bring about the decomposition to the hydrocarbon, which, being insoluble in water, has its presence made evident by the aqueous solution of the alcohol becoming cloudy.

The physical constants of the new hydrocarbon are compared with those of the isomeric benzene derivatives mesitylene, ψ-cumene and *p*-methylethylbenzene. Owing to the ease with which it undergoes polymerisation or rearrangement, the purification is a matter of great difficulty; it is best accomplished by rapid distillation in steam under reduced pressure.

The hydroaromatic hydrocarbon has a lower density, D_4^{20} 0·839, than its aromatic isomerides. Spectrochemically the high exaltation of

the specific refractive and dispersive powers of the hydrocarbon is of interest.

Unlike the chlorinated semibenzene, the hydrocarbon is only slowly changed by heat even at 160°, and the products are mainly condensation products, D_4^{20} 0·8837, n_D^{20} 1·51209.

Aromatic products were obtained by distilling the methylene derivative in hydrogen under reduced pressure, amongst which ψ-cumene was identified. It is undecided whether this is formed during distillation or at the time of decomposition of the hydroaromatic alcohol. The methylene derivative is immediately oxidised in the cold by potassium permanganate; it unites with bromine, but a mixture of products is formed. Several hydrocarbons are formed on reduction with sodium and moist ether. E. F. A.

Old and New Benzene Formulæ. ISRAEL LIFSCHITZ (*Zeitsch. angew. Chem.*, 1911, **24**, 1153—1161).—An account of the various structural formulæ which have been put forward for the benzene molecule. The author favours Werner's formula, but considers that it will be possible to combine it with that of Stark in such a way that all the various reactions and phenomena can be accounted for.

T. S. P.

Bromination of *cyclo*Hexane. F. BODROUX and FELIX TABOURY (*Bull. Soc. chim.*, 1911, [iv], **9**, 592—594. Compare Markownikoff, Abstr., 1898, i, 637).—In diffused sunlight bromine acts extremely slowly on *cyclo*hexane at its boiling point, but in direct sunlight the boiling hydrocarbon decolorises bromine rapidly, forming *cyclo*hexyl bromide and some polybromo-derivatives. In quartz vessels and exposed to ultra-violet rays from a mercury lamp, the hydrocarbon does not react with bromine. *cyclo*Hexyl bromide at the boiling point, 162°, reacts with bromine, forming some dibromo*cyclo*hexane, b. p. 144—145°/100 mm., which is probably the 1 : 2-isomeride. T. A. H.

Additive Compounds of *m*-Dinitrobenzene. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 46—47).—A solution of *m*-dinitrobenzene in aniline deposits on cooling red crystals, m. p. 41—42°, losing aniline on exposure to air. Similarly, dimethyl-*p*-toluidine yields a black, unstable compound, m. p. 43°. With α-naphthylamine in alcoholic solution are produced red needles, m. p. 57°. Similarly, dimethyl-β-naphthylamine gives dark red needles, m. p. 52—53°. Tetramethyl-*m*-phenylenediamine yields a very dark garnet-red substance, m. p. 58°. With benzidine are obtained black crystals, m. p. 128°, decomposed by hydrochloric acid. All the foregoing compounds contain an equal number of molecules of amine and dinitrobenzene.

4 : 4′-Tetramethyldiaminodiphenylmethane gives garnet-red plates or crystals, m. p. 76°, containing 2 mols. of amine per mol. of dinitrobenzene.

4 : 4′-Tetramethyldiamidobenzophenone in alcoholic solution gives red plates, m. p. 91°, containing 2 mols. of dinitrobenzene per mol. of the base. J. D. K.

Indene Series. RUDOLF WEISSGERBER (*Ber.*, 1911, **44**, 1436—1448). [With F. KRAFT.]—1-Alkyl derivatives of indene (compare Marckwald, Abstr., 1900, i, 434) can be prepared by the action of alkyl halides on sodioindene (Abstr., 1909, i, 219). As a rule, not readily volatile tarry products are also formed. With benzyl chloride and toluene a 30% yield of 1-benzylindene is obtained. It has b. p. 185°/18 mm., and crystallises from alcohol in yellow prisms, m. p. 33—34°.

[With P. BREHME.]—*Di-indene*, $C_{18}H_{16}$, can be obtained by boiling indene for ten to twenty-four hours with its own weight of glacial acetic acid; it has b. p. 235—245°/16 mm., and crystallises from glacial acetic acid in nodular masses, m. p. 51°. It is stable towards oxidising agents, and a quantitative yield can also be obtained by boiling indene for fifteen hours with syrupy phosphoric acid.

[With M. VOGEL, A. DOMBROWSKY, and F. KRAFT.]—A 75% yield of indene-1-carboxylic acid, $CH\Big\langle{C_6H_4 \atop CH}\Big\rangle CH\cdot CO_2H$, is obtained by passing dry carbon dioxide into the fused sodium indene from heavy benzene, and a theoretical yield by passing carbon dioxide into a xylene suspension of the finely divided sodioindene. It crystallises from toluene in needles, m. p. 156—157°, has b. p. 193—195°/12 mm. (compare Grignard and Courtot, this vol., i, 538), and differs entirely from the acid described by Perkin and Révay (Trans., 1894, **65**, 238). It combines with bromine slowly, and the additive *compound* has m. p. 136—137° (decomp.). The *methyl* ester, $C_{11}H_{10}O_2$, is a pale yellow oil, b. p. 153—154°/23 mm., with a fragrant odour; the *ethyl* ester has b. p. 164°/24 mm. When heated for several hours at 180° in an oil-bath, the acid yields *di-indenedicarboxylic acid*, $C_{20}H_{16}O_4$, which crystallises from boiling glacial acetic acid in compact needles, m. p. 265° (decomp.).

[With P. BREHME.]—Chlorohydroxyhydrindene (Spilker, Abstr., 1893, i, 519) is readily obtained by the addition of hypochlorous acid prepared by Wohl and Schweitzer's method (Abstr., 1907, i, 194) to indene.

Dihydroxyhydrindene, $C_6H_4\Big\langle{CH(OH) \atop CH_2}\Big\rangle CH\cdot OH$, obtained by heating the chlorohydroxy-derivative with potassium acetate and acetic anhydride and then hydrolysing with potassium hydroxide solution (D 1·3), crystallises from water in brilliant needles, m. p. 158°. The products described by Spilker, m. p. 120°, and by Heusler and Schieffer, m. p. 98—99° (Abstr., 1899, i, 365), are evidently impure. The glycol yields β-hydrindone when warmed with dilute sulphuric acid.

1-*Chlorohydrindene*, $C_6H_4\Big\langle{CHCl \atop CH_2}\Big\rangle CH_2$, is readily formed by passing hydrogen chloride into well cooled indene, and forms a colourless oil which reacts with the greatest readiness with water, yielding indene, 1-hydroxyhydrindene (compare König, Abstr., 1893, i, 587), and 1-hydrindyl ether. 1-Hydroxyhydrindene is odourless and crystallises with great readiness. The *methyl ether*, $C_9H_9\cdot OMe$, prepared by the action of sodium methoxide on the chloro-derivative, is a colourless oil with b. p. 98°/10 mm., and has an intense odour of acetal.

The *ethyl ether*, $C_{11}H_{14}O$, has b. p. 106—109°/16 mm., and 1-*acetoxyhydrindene*, $C_{11}H_{12}O_2$, has b. p. 135°/15 mm. or 241° under atmospheric pressure.

1-*Hydrindyl ether*, $(C_9H_9)_2O$, crystallises from alcohol and has m. p. 51—53°. J. J. S.

Ketens. XXIII. The Reactivity of Halogen Atoms Towards Metals. HERMANN STAUDINGER, KARL CLAR, and E. CZAKO (*Ber.*, 1911, 44, 1640—1647).—The authors have investigated the behaviour of several halogen derivatives of methane, and of benzyl chloride, benzylidene dichloride, ω-chlorodiphenylmethane, benzotrichloride, di-ω-chlorodiphenylmethane, and ω-chlorotriphenylmethane towards zinc in ethereal solution, and find that the removal of halogen takes place readily only in the case of the three compounds last mentioned. From these observations the conclusion is drawn that the substitution of hydrogen by phenyl or chlorine increases the reactivity of the halogen atom. The influence exerted by the chlorine atom is, however, less than that of the phenyl group.

The entrance of substituents into the phenyl groups considerably modifies the reactivity of the chlorine atoms in di-ω-chlorodiphenylmethane. Whilst di-ω-chloro-4 : 4′-dimethoxydiphenylmethane reacts with zinc even more vigorously than di-ω-chlorodiphenylmethane, di-ω-chlorodiphenylmethane-4 : 4′-dicarboxyl chloride and methyl di-ω-chlorodiphenylmethane-4 : 4′-dicarboxylate are without action towards this metal.

Attention is also called to the fact that acyl chlorides do not react with zinc in ethereal solution, and, therefore, contrary to the usual view, the chlorine atom must be firmly combined with the carbonyl group. A similar behaviour is exhibited by many other halogen compounds, in which the halogen is attached to an unsaturated carbon atom. The apparent mobility of the chlorine atom of acyl chlorides is due, not to its feeble attachment, but to the presence of the unsaturated carbonyl group, which readily combines with water, alcohol, and amines.

The interaction of acyl chlorides with these compounds is represented by the following scheme:

$$R\cdot COCl + H\cdot R' \longrightarrow OH\cdot CRR'Cl \longrightarrow R\cdot COR' + HCl.$$

It is also found that acyl chlorides do not react with magnesium to give Grignard compounds, and this is explained by the chlorine atom being firmly combined with the carbonyl group.

The method previously described (Staudinger, Abstr., 1908, i, 654) for the preparation of aldehydes by the action of magnesium on imino-chlorides has been extended to *iso*butyrophenylimino-chloride, diphenylacetophenylimino-chloride, and triphenylacetophenylimino-chloride, but in no case could a reaction either with magnesium or with zinc be induced. The halogen atom of imino-chlorides is, therefore, firmly attached to the C⁚N group, and its apparent mobility in many reactions is referred to the intermediate formation of additive compounds, according to the scheme:

$$R\cdot CCl⁚NPh + H\cdot R' \longrightarrow CRR'Cl\cdot NHPh \longrightarrow R\cdot CR'⁚NPh + HCl.$$

The greater reactivity of imino-chlorides, as compared with acyl chlorides, towards alcohol, water, and amines is due to the greater additive power of the C⁚N group.

Di-ω-chlorodiphenylmethane reacts vigorously with zinc in ethereal solution, yielding αβ-dichlorotetraphenylethane, $CPh_2Cl\cdot CPh_2Cl$, together with tetraphenylethylene; if the mixture is heated, tetraphenylethylene is the sole product. According to the authors, ω-chlorodiphenylmethyl is formed as an intermediate product in the reaction, but attempts to convert this into a peroxide by the passage of oxygen into the mixture during the reaction proved unsuccessful. Di-ω-chlorodiphenylmethane yields with zinc chloride a yellowish-green *additive* compound.

When treated with zinc in ethereal solution, benzotrichloride gives tolane dichloride (αβ-dichloro-*s*-diphenylethylene).

Di-ω-chloro-4 : 4′-*dimethoxydiphenylmethane*, obtained by the action of oxalyl chloride on dimethoxybenzophenone, has m. p. 101—102°, and gives with zinc chloride and mercuric chloride in ethereal solution red *additive* compounds, which are decomposed by water, yielding the original ketone. It reacts with zinc or mercury in ethereal solution, yielding 4 : 4′ : 4″ : 4‴-*tetramethoxytetraphenylethylene*.

Methyl di-ω-chlorodiphenylmethane-4 : 4′-*dicarboxylate*,

$$CCl_2(C_6H_4\cdot CO_2Me)_2,$$

prepared by the interaction of phosphorus pentachloride and methyl benzophenone-4 : 4′-dicarboxylate, crystallises in colourless needles, m. p. 73°.

iso*Butyrophenylimino-chloride*, $CHMe_2\cdot CCl⁚NPh$, prepared from phosphorus pentachloride and *iso*butyranilide, is a colourless liquid, b. p. 102—104°/11 mm.

Diphenylacetylphenylimino-chloride, $CHPh_2\cdot CCl⁚NPh$, forms colourless crystals, m. p. 90°.

Triphenylacetylphenylimino-chloride, $CPh_3\cdot CCl⁚NPh$, has m. p. 132°.

F. B.

Hydrogenation by means of Calcium and Alcohol. PIERRE BRETEAU (*Bull. Soc. Chim.*, 1911, [iv], 9, 585—586, and *J. Pharm. Chim.*, 1911, [vii], 3, 580—582).—The process depends on the utilisation of a reaction recorded by Doby (Abstr., 1903, i, 546), in which calcium reacts with ammonia to form hydrogen and calcium amide, the latter being then decomposed by alcohol, giving calcium ethoxide. The application of the method to phenanthrene, which is not reduced by calcium and alcohol alone, is as follows: Fifteen grams of calcium filings are placed in a litre flask provided with a reflux condenser. To this are added 5 grams of phenanthrene in 200 c.c. of alcohol, and the mixture is heated to boiling. Dry ammonia gas is then led into the mixture, and the flame extinguished as soon as hydrogen begins to be evolved. After the calcium is dissolved, the solution is boiled during one hour and then acidified with dilute hydrochloric acid. On cooling, tetrahydrophenanthrene separates as an oil, and may be separated and purified by distillation.

T. A. H.

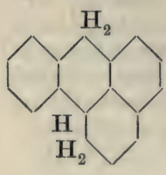
Phenanthrene Series. XXXI. Nitro- and Amino-phenanthrenes. JULIUS SCHMIDT and EUGEN HEINLE (*Ber.*, 1911, **44**, 1488—1503).—1-Nitrophenanthrene has not yet been prepared. The four other possible isomerides are produced by the addition of a mixture of acetic anhydride and nitric acid, D 1·45, to a solution of phenanthrene in hot glacial acetic acid. The separation of the four compounds necessitates a tedious fractional crystallisation from alcohol, whereby 60% of pure 9-nitrophenanthrene, 2% of pure 3-nitrophenanthrene, and 20% each of approximately pure 2-*nitrophenanthrene*, m. p. 99°, and 4-*nitrophenanthrene*, m. p. 80—82°, are obtained, the yields being calculated on the crude nitrophenanthrenes; a very small amount of 2-nitrofluorene, produced from a trace of fluorene in the phenanthrene, has also been isolated. 2-Nitrophenanthrene crystallises in pale yellow rosettes, and yields 2-nitrophenanthraquinone when oxidised by chromic and acetic acids. 4-Nitrophenanthrene crystallises in yellow needles, and is oxidised to 4-nitrophenanthraquinone.

A methyl-alcoholic solution of 9-nitrophenanthrene is reduced by zinc dust and methyl-alcoholic ammonia, yielding two modifications of 9-aminophenanthrene, which are separated by crystallisation from alcohol. The less soluble α-form, m. p. 137—138°, which is the principal product, has been described by Schmidt and Strobel (Abstr., 1903, i, 691). The β-modification, m. p. 104°, forms a benzoyl derivative, m. p. 199°, identical with that obtained from the α-modification, yields 9-phenanthrylphenylcarbamide with phenylcarbimide much more slowly than does the α-modification, and is converted into the α-modification by acetylation and subsequent hydrolysis. The suggestion is made that the isomerism of the two modifications is due to the different distributions of the double linkings in the phenanthrene nucleus. In large quantities, 9-nitrophenanthrene is reduced most conveniently by tin and hydrochloric acid. 9-Aminophenanthrene forms a *picrolonate*, $C_{14}H_{11}N,C_{18}H_8O_5N_4$, m. p. 230—231° (decomp.), and a *perchlorate*, m. p. 185°.

4-*Aminophenanthrene*, m. p. 105°, obtained by reducing 4-nitrophenanthrene with stannous chloride and acetic acid, does not exist in two modifications, and forms a *hydrochloride*, *picrate*, m. p. 216° (decomp.), *picrolonate*, m. p. 195°, decomp. 232°, *benzoyl* derivative, m. p. 224°, and *acetyl* derivative, m. p. 190°; with ethereal phenylcarbimide, it yields s-*phenyl*-4-*phenanthrylcarbamide*, $C_{14}H_9\cdot NH\cdot CO\cdot NHPh$, m. p. 219—220°, resolidifying and subsequently melting at 279—280°.

C. S.

Identity of Graebe's *iso*Chrysofluorene with Dihydrobenzanthrene. ROLAND SCHOLL and CHRISTIAN SEER (*Ber.*, 1911, **44**, 1671—1674).—Graebe's "*iso*chrysofluorene" (Abstr., 1894, i, 336), obtained by pyrogenic synthesis from 1-benzylnaphthalene, has the formula $C_{17}H_{14}$, and not $C_{17}H_{12}$. After purification by means of the picrate, it has m. p. 79—80°, and is identical with dihydrobenzanthrene (annexed formula: see this vol., i, 676). The red oxidation



product described by Graebe is probably a mixture of benzanthrone and anthraquinone-1-carboxylic acid. F. B.

New Method of Preparation of Benzylamine and Hexahydrobenzylamine. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1911, **153**, 160—162).—The authors' method of preparing amines from aliphatic alcohols (Abstr., 1909, i, 292) has been applied by heating the vapour of benzyl alcohol and ammonia in the presence of thorium dioxide; at 330°, benzylamine is the chief product; at 370—380°, dibenzylamine. In practice, a resinous hydrocarbon is gradually deposited on the oxide, and the reaction must be interrupted from time to time in order to revive the catalyst by heating it at a dark red heat in the air.

When the vapour of the benzylamine produced by this method is passed, together with hydrogen, over nickel at 170—180°, considerable quantities of ammonia and toluene are formed, but also a fairly good yield of hexahydrobenzylamine is obtained, identical with that obtained by Démianoff. The experiment fails with benzylamine produced by other methods, probably owing to traces of impurities which destroy the activity of the catalyst. C. S.

Preparation of Sulphonated Naphthalene Derivatives. KALLE & Co. (D.R.-P. 233934).—When naphthalenepolysulphonic acids are boiled with zinc dust in aqueous solution (preferably in the presence of alkali or ammonium chloride), the sulphonic groups which would be attacked in the case of an alkali fusion are eliminated and replaced by hydrogen. By this means α-naphthylamine-3 : 6 : 8-trisulphonic acid yielded the 3 : 6-disulphonic acid; α-naphthylamine-4 : 6 : 8-trisulphonic acid, the 4 : 6-disulphonic acid; α-naphthylamine-3 : 5 : 7-trisulphonic acid, the 3 : 7-disulphonic acid; α-naphthylamine-2 : 5 : 7-trisulphonic acid, the 2 : 7-disulphonic acid; β-naphthylamine-3 : 6 : 8-trisulphonic acid was converted into the 3 : 6-disulphonic acid; α-naphthol-3 : 5 : 7-trisulphonic acid into 3 : 7-disulphonic acid; α-naphthylamine-3 : 8-disulphonic acid into 3-monosulphonic acid; α-naphthylamine-4 : 8-disulphonic acid yielded naphthionic acid; β-naphthylamine-4 : 8-disulphonic acid a mixture of the 4- and the 8-monosulphonic acids; and α-naphthol-8-amino-4 : 6-disulphonic acid, the α-naphthol-8-amino-6-sulphonic acid. F. M. G. M.

Preparation of Sulphonated Aromatic Ammonium Compounds. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 233328).—The sulphonation of aromatic quaternary ammonium bases yields crystalline compounds soluble in water, which probably have the constitution of inner anhydrides.

Phenylnaphthylmethyldimethylammonium chloride, m. p. 124°, prepared from dimethylaniline and ω-chloro-β-methylnaphthalene, yields a crystalline *sulphonic acid*.

Phenylbenzyldimethylammonium hydroxide sulphonic anhydride, large, colourless crystals, is obtained by treating a cooled solution of

phenylbenzyldimethylammonium chloride in concentrated sulphuric acid with fuming acid (23% SO_3), and heating the mixture at 25—30°; when acid containing 70% SO_3 is employed, a somewhat soluble *disulphonic acid* is produced.

When the *phenylbenzyldimethylammonium hydroxide sulphonic anhydride* prepared from benzyl chloride and dimethylaniline-*m*-sulphonic acid is sulphonated, an isomeric disulphonic acid is obtained.

F. M. G. M.

The Influence of the Medium and of Light on the Rate of Decomposition of Quaternary Ammonium Salts. EDGAR WEDEKIND, F. PASCHKE, and, in part, W. MAYER (*Ber.*, 1911, **44**, 1406—1415. Compare Abstr., 1908, i, 723).—The racemisation of *d*-phenylbenzylmethylpropylammonium bromide in chloroform and in chloroform mixed with other solvents has been studied.

The addition of 20% of a hydroxylic compound, such as methyl or ethyl alcohol, retards racemisation, as does acetone, whereas benzene and carbon disulphide favour decomposition. Solutions of phenylbenzylmethylethylammonium bromide in mixtures of ethyl alcohol and chloroform, or of ethyl alcohol and ethylene dibromide, have smaller electrical conductivities than solutions of the same concentration in ethyl alcohol alone.

The fact that the racemisation is less in hydroxylic solvents is probably due to the fact that in such solvents the salts are largely ionised, and that for racemisation (thermal dissociation) complete molecules are necessary. Labile salts, such as *l*-phenylbenzylmethyl (methylanilinoethyl) ammonium iodide (Wedekind and Mayer, Abstr., 1909, i, 186), can undergo decomposition in ionising media, but the reaction here is less rapid than in such solvents as chloroform. The reaction has been studied by both polarimetric and electrical conductivity determinations, and the results indicate that autoracemisation is to be attributed to a decomposition into tertiary amine and alkyl halide: $C_7H_7\cdot NMePh\cdot CH_2\cdot CH_2\cdot NMePh^{\cdot} + I' \rightleftarrows C_7H_7\cdot NMePhI\cdot CH_2\cdot CH_2\cdot NMePh \rightleftarrows C_7H_7I + NMePh\cdot CH_2\cdot CH_2\cdot NMePh$.

In determining the molecular conductivity it was noticed that the value for this fell to a minimum after about 103 hours, and then increased again, until after 1650 hours the original value was again reached. This is probably due to the fact that the benzyl iodide formed reacts with the solvent alcohol, forming hydrogen iodide and benzyl ethyl ether (compare Halban, Abstr., 1909, i, 627). The solid quaternary ammonium iodide also decomposes when kept, it loses in weight, owing to evolution of benzyl iodide, and its optical activity diminishes from $-95{\cdot}98°$ to $-91{\cdot}07°$ after 230 days.

The accelerating influence of light on the racemisation of quaternary ammonium salts appears to be of a purely thermal and non-actinic nature (compare Abstr., 1906, i, 419).

When a solution of *d*-phenylbenzylmethylallylammonium hydroxide in chloroform and a little alcohol is kept for forty-eight hours, a slight diminution in the rotation is observable (compare Abstr., 1905, i, 520). This is attributed, not to the decomposition of the base itself, but of a

small amount of quaternary chloride formed by the reaction of the base with the chloroform. J. J. S.

Preparation of Hydroxyphenylethyldialkylamines. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 233069. Compare Abstr., 1906, i, 204, 761, 979; 1907, i, 151, 234, 336).—When the quaternary ammonium salts of *p*-hydroxyphenylethylamines are distilled, they furnish hydroxyphenylethyldialkylamines, and thus confirm the work of Gaebel and Léger, who formulated hordenine as β-*p*-hydroxyphenylethyldimethylamine (Abstr., 1907, i, 151); in the present instance hordenine methiodide, m. p. 230° (prepared from *p*-hydroxyphenylethylamine), furnished on distillation hordenine identical with the product described by these authors.

Hordenine methochloride has m. p. 285° (decomp.).

m-*Ethoxyphenylethylamine hydrochloride*, m. p. 160—165° (prepared from *m*-ethoxyphenylpropionamide and sodium hypochlorite), when heated at 100° with alcoholic sodium hydroxide and methyl chloride yields m-*ethoxyphenylethyltrimethylammonium chloride*, m. p. 130°; the *methiodide* forms colourless needles, m. p. 185—190°, and on distillation in a vacuum furnishes a quantitative yield of m-*ethoxyphenylethyldimethylamine*, a colourless liquid, b. p. 130—133°/15 mm., and convertible by the action of hydrogen iodide into m-*hydroxyphenylethyldimethylamine*, m. p. 103°. F. M. G. M.

Preparation of Hydroxyphenylethylamines and their Alkyl Ethers. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 233551).—It is found that Hofmann's reaction for the conversion of amides into amines can be applied for the preparation of hydroxyphenylethylamines from hydroxyphenylpropionic acids.

β-*p*-Methoxyphenylpropionic acid, $OMe\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO_2H$, was converted by known methods into p-*methoxyphenylpropionamide*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2$, needles, m. p. 120°, which by treatment with sodium hypochlorite yielded *p*-methoxyphenylethylamine (its hydrochloride has m. p. 210°), and was subsequently converted with hydrogen iodide into *p*-hydroxyphenylethylamine.

Ethyl β-p-*hydroxyphenylpropionate*, m. p. 45°, b. p. 185°/13 mm., furnished an *amide*, m. p. 125°, and subsequently β-*p*-hydroxyphenylethylamine.

m-*Ethoxyphenylethylamine hydrochloride* has m. p. 160—165°, and m-*hydroxyphenylethylamine hydrochloride*, m. p. 145°.

o-*Ethoxyphenylethylamine* and o-*hydroxyphenylethylamine hydrochloride* have m. p. 210° and m. p. 155° respectively. F. M. G. M.

The Separation of 6-Chloro-*m*-cresol by the Chlorination of Pure *m*-Cresol, or of the Technical Mixture of *m*- and *p*-Cresols. ARTHUR LIEBRECHT (D.R.-P. 233118. Compare this vol., i, 537).—Pure 6-chloro-*m*-cresol can be isolated from the technical mixture of *m*- and *p*-cresol by chlorination and subsequent sulphonation of the mixed products with sulphuric acid at 100°. Any 3-chloro-*p*-cresol obtained in the first operation escapes sulphonation, whilst the sulphonated 6-chloro-*m*-cresol is separated in the form of

its sparingly soluble sodium salt, and the sulphonic group eliminated by known methods. F. M. G. M.

Preparation of 6-Amino-α-naphthol-5-sulphonic Acid. KALLE & Co. (D.R.-P. 233105).—β-Naphthylamine-1 : 5-disulphonic acid (prepared by further sulphonation of β-naphthylamine-1-sulphonic acid) when fused at 210—230° with potassium hydroxide yields 6-*amino-α-naphthol-5-sulphonic acid*, which crystallises from water in slender needles or compact crystals and combines very readily (in alkaline solution) with diazonium salts; its solution in sodium carbonate exhibits a green fluorescence. F. M. G. M.

Preparation of Sulphaminobenzoylaminonaphthols and their Sulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 233117).—Sulphaminobenzoylaminonaphthols, prepared by the action of sulphurous acid on the salts of the corresponding nitrobenzoylaminonaphthols, are readily converted by dilute mineral acid into the corresponding aminobenzoylaminonaphthols; this reaction is capable of extended application, and can be successfully employed in the case of substituted halogen derivatives.

Details for the preparation of sulphaminobenzoyl-5-amino-β-naphthol (from *m*-nitrobenzoyl-1 : 6-aminonaphthol) and of *p*-sulphaminobenzoyl-6-amino-α-naphthol-7-sulphonic acid are given in the patent.

F. M. G. M.

Preparation of Phenyl Esters of Iodoparaffin Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 233327).—*Phenyl iodoacetate*, glistening needles, m. p. 75—77°, is prepared by boiling together iodoacetic acid, phenol, and carbonyl chloride in benzene-pyridine solution.

Thymol iodoacetate, b. p. 176—178°/10 mm., is an oil at the ordinary temperature.

*Guaiacol α-bromo*iso*valerate*, colourless, odourless, tasteless crystals, has m. p. 69—70°, and when boiled with potassium iodide yields *guaiacol α-iodo*iso*valerate*, m. p. 76—79°.

*Tolyl α-iodo*iso*valerate* is a viscous, oily fluid which slowly solidifies.

Guaiacol α-iodo-β-methylhexoate, $C_3H_7 \cdot CHMe \cdot CHI \cdot CO_2 \cdot C_6H_4 \cdot OMe$, and its *bromo*-analogue form oily, yellow, tasteless, odourless, fluids. *Guaiacol α-iodo*-n-*butyrate* has b. p. 185°/10 mm., and *guaiacol α-bromo*-n-*butyrate*, b. p. 165°/10 mm.

Guaiacol iodobehenate, a thick, honey-like oil, is prepared from iodobehenic acid and guaiacol in the presence of phosphorus trichloride.

*Quinol di-α-bromo*iso*valerate*, $(C_4H_8Br \cdot CO_2)_2C_6H_4$, odourless, tasteless needles, has m. p. 53°; *quinol di-α-iodo*iso*valerate* has similar properties and m. p. 85—87°.

Guaiacol iodostearate is a yellowish-red oil, and *guaiacol α-iodo*iso*butyrate* has b. p. 160—175°/15 mm. These compounds are of therapeutic value. F. M. G. M.

Naphtharesorcinol [1 : 3-Dihydroxynaphthalene] and 4-Amino-β-naphthol. RICHARD MEYER and KURT WOLFSLEBEN (*Ber.*, 1911, **44**, 1958—1966).—An account of the preparation and properties of some derivatives of 1 : 3-dihydroxynaphthalene and of 4-amino-β-naphthol, obtained in an unsuccessful attempt to prepare a meta-quinone of the naphthalene series.

When 1 : 3-dihydroxynaphthalene (1 mol.) is treated with bromine (4 atoms) in glacial acetic acid solution at a low temperature, 2 : 4-*dibromo*-1 : 3-*dihydroxynaphthalene*, $C_{10}H_4Br_2(OH)_2$, crystallising in needles, m. p. 128—129°, is produced; the *acetyl* derivative, $C_{10}H_4Br_2(OAc)_2$, has m. p. 125°.

Tribromo-1 : 3-*dihydroxynaphthalene*, $C_{10}H_3Br_3(OH)_2$, prepared by the action of bromine (8 atoms) on 1 : 3-dihydroxynaphthalene in a similar manner, crystallises in silvery needles, m. p. 186°; the *acetyl* derivative, $C_{10}H_3Br_3(OAc)_2$, crystallises in needles or prisms of a monoclinic habit, m. p. 182°; the *benzoyl* derivative, felted needles, has m. p. 129° (not sharp).

When the bromination is carried out in the presence of water at 0°, an *isomeride* having the constitution $\begin{matrix} C_6H_4\cdot C(OH) \\ | \\ CBr_2 \text{———} CO \end{matrix}\!\!>\!CBr$ or

$$\begin{matrix} C_6H_4 \text{———} CO \\ | \\ CBr_2\cdot C(OH) \end{matrix}\!\!>\!CBr$$

is obtained. This forms yellow crystals, m. p. 85° (decomp.), and when heated with acetyl chloride loses bromine and yields the above-mentioned acetyl derivative of 2 : 4-dibromo-1 : 3-dihydroxynaphthalene.

Zincke and Egly's 2 : 4-tetrachloro-1 : 3-diketotetrahydronaphthalene (Abstr., 1898, i, 439) is obtained by the action of chlorine on 1 : 3-dihydroxynaphthalene in glacial acetic acid solution.

When air is passed through an alkaline solution of 1 : 3-dihydroxynaphthalene, β-hydroxy-α-naphthaquinone is produced.

Attempts to oxidise substituted derivatives of 1 : 3-dihydroxynaphthalene yielded tarry products.

4-*Benzoylamino-β-naphthyl benzoate*, $NHBz\cdot C_{10}H_6\cdot OBz$, forms colourless needles, m. p. 188°.

Ethyl 3-hydroxy-α-naphthyloxamate, $OH\cdot C_{10}H_6\cdot NH\cdot CO\cdot CO_2Et$, prepared by the interaction of 4-amino-β-naphthol and ethyl oxalate, crystallises in pale yellow, felted needles, m. p. 171°. When hydrolysed with aqueous sodium hydroxide, this yields *3-hydroxy-α-naphthyloxamic acid*, which crystallises in stellar aggregates of needles, m. p. 219° (decomp.); the *amide*, $OH\cdot C_{10}H_6\cdot NH\cdot CO\cdot CO\cdot NH_2$, forms yellow, flat needles, m. p. 260°.

N-3-*Hydroxy-α-naphthylphthalamic acid*,

$$OH\cdot C_{10}H_6\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H,$$

obtained by heating 4-amino-β-naphthol with phthalic anhydride in xylene solution, has m. p. 220° (decomp.).

N-α-Naphthylphthalamic acid, $C_{10}H_7\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$, and *N*-β-naphthylphthalamic acid may be prepared from the corresponding naphthylamines in a similar manner (compare Piutti, Abstr., 1886, 472, 473).

1(or 3)-*Bromo-4-benzoylamino-β-naphthyl benzoate*,

$$NHBz\cdot C_{10}H_5Br\cdot OBz,$$

obtained by brominating the benzoyl derivative of 4-amino-β-naphthol in alcoholic solution, forms colourless crystals.

1 : 3-*Dibromo-4-acetylamino-β-naphthol*, $NHAc\cdot C_6H_4Br_2\cdot OH$, is prepared by the interaction of bromine and 4-acetylamino-β-naphthol in glacial acetic acid solution; it crystallises in stout needles, m. p. 210° (decomp.), and on treatment with acetic anhydride and a little sulphuric acid yields 1 : 3-*dibromo-4-acetylamino-β-naphthyl acetate*, $NHAc\cdot C_6H_4Br_2\cdot OAc$, m. p. 230°, which is also obtained by brominating and subsequently acetylating 4-amino-β-naphthol. F. B.

Action of Phenol on Methylcoumaric Acid Dibromide and the Constitution of Werner's "Hydroxyphenylcoumaran." RICHARD STOERMER and C. FRIEMEL (*Ber.*, 1911, **44**, 1838—1853. Compare Werner, Abstr., 1906, i, 180).—The supposed 2-hydroxyphenylcoumaran, $C_6H_4<\begin{matrix}O\cdot CH_2\\ \vert \\ CH\cdot C_6H_4\cdot OH\end{matrix}$, prepared by Werner (*loc. cit.*) by the action of phenol on methylcoumaric acid dibromide, is shown to be 4′-*hydroxy-2-methoxystilbene*, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_4\cdot OH$. On oxidation, *o*-methoxybenzoic acid and anisic acid are formed. The chief product of the interaction of the dibromide and phenol is β-bromo-α-methoxyphenylhydrocoumaric acid. This amounts to 65%; some is decomposed into hydroxystilbene during the reaction, and it is readily converted into this by treatment with sodium carbonate.

The constitution of 4′-hydroxy-2-methoxystilbene is established by its synthesis from *p*-hydroxyphenylacetic acid and *o*-methoxybenzaldehyde; these condense to hydroxymethoxystilbenecarboxylic acid, which is heated with soda lime.

4′-*Hydroxy-2-methoxystilbene*, $C_{15}H_{14}O_2$, regarded by Werner as hydroxyphenylcoumaran, $C_{14}H_{12}O_2$, is prepared by mixing equal parts of methylcoumaric acid dibromide and phenol and heating on the water-bath; it has m. p. sharp at 149°.

β-Bromo-α-methoxyphenylhydrocoumaric acid,

$$OMe\cdot C_6H_4\cdot CHBr\cdot CH(C_6H_4\cdot OH)\cdot CO_2H,$$

crystallises in colourless, rhombic plates, m. p. 185—186°.

2 : 4′-Dimethoxystilbene, obtained by the action of methyl sulphate on the monomethyl ether, forms blue fluorescing platelets, m. p. 93° (compare Werner, *loc. cit.*).

2-*Methoxy-4′-ethoxystilbene* crystallises in blue, fluorescing, broad needles, m. p. 70°.

4′-*Benzoyloxy-2-methoxystilbene* separates in colourless needles of silky lustre, m. p. 123°. The corresponding p-*nitrobenzoyl* derivative forms lustrous, golden-yellow plates, m. p. 148°.

The *dibromide* of the above dimethoxy-derivative is a colourless powder, m. p. 133°; the *dibromide* of the acetyl derivative crystallises in small, colourless plates, m. p. 170°.

On reduction of dimethoxystilbene in alcohol with sodium, 2 : 4′-*dimethoxydibenzyl* is obtained as a clear, transparent oil, which becomes solid in ice, m. p. 45°.

The reduction of methoxyhydroxystilbene is more difficult, and is

carried out in amyl alcohol. 4′-*Hydroxy-2-methoxydibenzyl* forms colourless, long needles, m. p. 63°. Methyl sulphate converts it into the dimethyl ether, m. p. 45°. The p-*nitrobenzoyl ether* crystallises in creamy-yellow plates, m. p. 135°.

Oxidation of both methoxyhydroxystilbene and its dihydro-derivative with permanganate gave *o*-methoxybenzoic acid; the oxidation of the dimethoxystilbene gave a mixture of *o*- and *p*-methoxybenzoic acids.

p-*Methoxy-α-*o*-anisylcinnamic acid*,

$$OMe\cdot C_6H_4\cdot C(CO_2H){:}CH\cdot C_6H_4\cdot OMe,$$

prepared by the Perkin synthesis from anisaldehyde and sodium *o*-methoxyphenylacetate, crystallises in colourless needles, m. p. 191°. On distillation with soda lime, 2 : 4′-dimethoxystilbene is obtained.

α-p-*Methoxyphenylcoumaric acid*, $OMe\cdot C_6H_4\cdot CH{:}C(C_6H_4\cdot OH)\cdot CO_2H$, from sodium *p*-hydroxyphenylacetate and *o*-methoxybenzaldehyde, crystallises in renniform aggregates of needles, m. p. 202°. On distillation with soda lime, methoxyhydroxystilbene, m. p. 149°, is obtained. Methyl sulphate converts it into the di-ether, and, on hydrolysis, *α-p*-methoxymethylcoumaric acid, m. p. 198°, is formed.

On condensation of ethylcoumaric acid dibromide with phenol, *β-bromo-α-ethoxyphenylhydrocoumaric acid*,

$$OEt\cdot C_6H_4\cdot CHBr\cdot CH(C_6H_4\cdot OH)\cdot CO_2H,$$

is obtained, crystallising in needles, m. p. 166°. On treatment with sodium carbonate, 4′-*hydroxy-2-ethoxystilbene* is obtained; it crystallises in blue, fluorescing needles, m. p. 107°. The compound 2-*methoxy* forms short, blue, fluorescing plates, m. p. 60°. E. F. A.

Syntheses by means of Sunlight. HEINRICH KLINGER [with WALTER ROERDANSZ] (*Annalen*, 1911, **382**, 211—221. Compare Klinger and Standke, Abstr., 1891, 900; Klinger and Kolvenbach, 1898, i, 467).—Valeroylquinol and benzoylquinol can be prepared by the action of zinc chloride on quinol and valeric or benzoic acid. The yields, however, are not good, as appreciable amounts of dark-coloured products are also formed. The dibenzoyl derivative of quinol, $C_6H_4(O\cdot COPh)_2$, is also formed when benzoic acid is used.

Mixtures of phenanthraquinone, benzene, and various aldehydes when exposed to bright sunlight in narrow sealed tubes undergo condensation. Most of the experiments were conducted in tubes 70 cm. long and 2 cm. wide.

Phenanthraquinone (10 grams), salicylaldehyde (6 c.c.), and benzene (50 c.c.) at the end of twenty days yield the *monosalicyloyl* derivative of phenanthraquinol, $C_6H_4{<}{\substack{C(OH)\\ C_6H_4}}{>}C\cdot O\cdot CO\cdot C_6H_4\cdot OH$, which crystallises from benzene or alcohol in colourless, glistening needles, m. p. 188°. It is hydrolysed by alkalis to the quinol, and this, on shaking in contact with air and the alkaline liquid, gives the quinone. The *diacetyl* derivative, $C_6H_4{<}{\substack{C(OAc)\\ C_6H_4}}{>}C\cdot CO\cdot C_6H_4\cdot OAc$, crystallises from a mixture of alcohol and benzene in well-developed, strongly refractive octahedra, m. p. 143°, or from hot alcohol in colourless, glistening needles, m. p. 151°. The corresponding *dibenzoyl* derivative, $C_{35}H_{22}O_5$, prepared by heating the salicyloylphenanthraquinol with five times

its weight of benzoic anhydride at 150—160° for thirty minutes, crystallises from benzene or glacial acetic acid in colourless, flat needles, m. p. 216—217°. Cold anhydrous nitric acid reacts with the salicyloyl derivative, yielding phenanthraquinone and 3 : 5-dinitrosalicylic acid.

Phenanthraquinone, cinnamaldehyde, and benzene, at the end of fourteen days, yield the *monocinnamoyl* derivative,

$$C_6H_4{<}\begin{matrix}C(OH)\\C_6H_4\end{matrix}{>}C{\cdot}O{\cdot}CO{\cdot}CH{:}CHPh,$$

which crystallises from benzene or glacial acetic acid in colourless needles, m. p. 193°, or from alcohol in canary-yellow needles. Its *acetyl* derivative, $\begin{matrix}C_6H_4{\cdot}C{\cdot}OAc\\ | \quad\;\; ||\\ C_6H_4{\cdot}C{\cdot}O{\cdot}CO{\cdot}CH{:}CHPh\end{matrix}$, crystallises in colourless prisms, m. p. 154°, and yields a *dibromide*, $C_{25}H_{18}O_4Br_2$, in the form of colourless, slender needles, m. p. 211°. The corresponding *benzoyl* derivative, $C_{50}H_{20}O_4$, forms colourless crystals, m. p. 218°.

The *monoanisoyl* derivative of phenanthraquinol,

$$C_6H_4{<}\begin{matrix}C(OH)\\C_6H_4\end{matrix}{>}C{\cdot}O{\cdot}CO{\cdot}C_6H_4{\cdot}OMe,$$

crystallises from benzene in slender, glistening plates, m. p. 232°, and yields an *acetyl* derivative, $C_{24}H_{18}O_5$, in the form of colourless, rhombic plates, m. p. 175°, and a *benzoyl* derivative, $C_{29}H_{20}O_5$, m. p. 193°.

Monofurfuroylphenanthraquinol, $C_{19}H_{12}O_4$, crystallises from benzene in well-developed, ruby-red prisms, m. p. 193°, or in orange-coloured crystals with the same m. p. The crystals have $a : c = 1 : 0{\cdot}3111$.

J. J. S.

New Derivatives in the Triphenylmethane Series. TIBOR SZÉKI (*Ber.*, 1911, **44**, 1476—1481).—In consequence of the labile character of the hydrogen atom in the para- position to a methoxy-group in hydroxyquinol trimethyl ether (Abstr., 1907, i, 45; 1910, i, 837), the ether condenses readily with aromatic aldehydes to form derivatives of triphenylmethane of the type $CHR[C_6H_2(OMe)_3]_2$. The condensation is effected in glacial acetic acid by hydrochloric acid, D 1·19, at the ordinary temperature. Thus benzaldehyde, *m*-nitrobenzaldehyde, and *p*-nitrobenzaldehyde respectively yield 2 : 4 : 5 : 2′ : 4′ : 5′-*hexamethoxytriphenylmethane*,

$$CHPh[C_6H_2(OMe)_3]_2,$$

m. p. 130·5°, 3-*nitro*-2′ : 4′ : 5′ : 2″ : 4″ : 5″-*hexamethoxytriphenylmethane*, m. p. 117°, citron-yellow needles, and 4-*nitro*-2′ : 4′ : 5′ : 2″ : 4″ : 5″-*hexamethoxytriphenylmethane*, m. p. 117°, citron-yellow crystals. The following compounds have been obtained from vanillin, salicylaldehyde, *p*-hydroxybenzaldehyde, piperonal, and protocatechualdehyde respectively: 4-*hydroxy*-3 : 2′ : 4′ : 5′ : 2″ : 4″ : 5″-*heptamethoxytriphenylmethane*, m. p. 187·5°; 2-*hydroxy*-2′ : 4′ : 5′ : 2″ : 4″ : 5″-*hexamethoxytriphenylmethane*, m. p. 176° (*acetate*, m. p. 148—149°); 4-*hydroxy*-2′ : 4′ : 5′ : 2″ : 4″ : 5″-*hexamethoxytriphenylmethane*, m. p. 205°; 3 : 4-*methylenedioxy*-2′ : 4′ : 5′ : 2″ : 4″ : 5″-*hexamethoxytriphenylmethane*, m. p. 137°; 3 : 4-*dihydroxy*-2′ : 4′ : 5′ : 2″ : 4″ : 5″-*hexamethoxytriphenylmethane*, m. p. 202° (*diacetate*, m. p. 124°).

The preceding compounds, excepting those prepared from the nitrobenzaldehydes and salicylaldehyde, react with bromine in benzene to form bromotrimethoxybenzene and brown or bluish-violet substances, which are very probably derivatives of diphenylmethane. C. S.

Transformations of *cyclo*Propyldimethylcarbinol. NICOLAI M. KIJNER and W. KLAWIKORDOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 595—608).—In the synthesis of *cyclo*propyldimethylcarbinol by the action of magnesium methyl iodide on ethyl *cyclo*propylcarboxylate (compare Zelinsky, Abstr., 1901, i, 660; 1902, i, 70), an appreciable proportion of an unsaturated *iodide*, $C_6H_{11}I$, b. p. 176—180°/752 mm. (decomp.), D_0^{20} 1·4305, is obtained. When freed from all traces of this iodide, *cyclo*propyldimethylcarbinol has b. p. 124·5—125°/752 mm., D_0^{20} 0·8844, n_D^{20} 1·4330 (compare Bruylants, Abstr., 1909, i, 226).

The hydrocarbon obtained by Alexéeff (Abstr., 1905, i, 639) by the action of acetic anhydride on *cyclo*propyldimethylcarbinol, and described by this author as dimethylmethylenetrimethylene, is found to be *β-cyclopropyl-Δ^α-propylene*, $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>CH\cdot CMe{:}CH_2$, b. p. 71·1—71·5°/772 mm., D_0^{20} 0·7523, n_D^{20} 1·4252, and is accompanied by acetyl derivatives giving on hydrolysis a mixture of alcohols, b. p. 124—160°, the nature of which was not investigated. Oxidation of this hydrocarbon by means of permanganate yields: (1) acetyltrimethylene; (2) *α-hydroxy-α-cyclopropylpropionic acid*,

$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>CH\cdot CMe(OH)\cdot CO_2H,$$

which forms colourless, acicular needles, m. p. 75·5°, gives a *hydrate*, $2C_6H_{10}O_3,H_2O$, m. p. 54—55°. This oxidation probably takes place according to the scheme:

$$C_3H_5\cdot CMe{:}CH_2 \longrightarrow C_3H_5\cdot CMe(OH)\cdot CH_2\cdot OH \longrightarrow$$
$$C_3H_5\cdot CMe(OH)\cdot CO_2H \longrightarrow C_3H_5\cdot COMe.$$

By the action of fuming hydrobromic acid, hydroxy*cyclo*propylpropionic acid yields (1) in the cold, *α-methylene-δ-bromovaleric acid*, $CH_2Br\cdot CH_2\cdot CH_2\cdot C({:}CH_2)\cdot CO_2H$, colourless, rhombic plates, m. p. 68°; (2) in a sealed tube at 100°, *δ-bromo-α-bromomethylvaleric acid*, $CH_2Br\cdot CH_2\cdot CH_2\cdot CH(CH_2Br)\cdot CO_2H$, plates, m. p. 88—90°.

When heated with dilute sulphuric acid in a sealed tube, *β-cyclo*propyl-Δ^α-propylene yields the hexylene oxide obtained by Zelinsky (Abstr., 1902, i, 70). Treatment of this oxide or of *cyclo*propyldimethylcarbinol by fuming hydrobromic acid yields *βε-dibromo-β-methylpentane*, $CH_2Br\cdot CH_2\cdot CH_2\cdot CMe_2Br$, b. p. 104—104·5°/23 mm., D_0^{20} 1·5865—1·5902, n_D^{20} 1·5045—1·5051. The action of alcoholic potassium hydroxide on this dibromo-derivative yields:

(1) *δ-Methyl-Δ^{αγ}-pentadiene*, $CH_2{:}CH\cdot CH{:}CMe_2$, b. p. 76—77·5°/766 mm., D_0^{20} 0·7193, n_D^{20} 1·4491. The structure of this hydrocarbon is decided by the considerable excess of the experimental (30·59) value of the molecular refraction over the calculated value (28·93) (compare Brühl, Trans., 1907, 115; Reif, Abstr., 1908, i, 847). δ-Methyl-Δ^{αγ}-pentadiene is found to be identical with the compound described by Bruylants (*loc. cit.*) as *β-cyclo*propylpropylene.

(2) *ε-Ethoxy-β-methyl-Δ^{β}-amylene*, $OEt\cdot CH_2\cdot CH_2\cdot CH\colon CMe_2$, b. p. 142·5—143·5°/766 mm., D_0^{20} 0·7975, n_D^{20} 1·4182. On oxidation with permanganate, it yields acetone and other products.

The action of hydriodic acid on *cyclo*propyldimethylcarbinol and reduction of the iodo-derivative thus obtained by means of sodium yields β-methylpentane. T. H. P.

Dehydration of Alkyl- and Benzylphenyl-*tert.*-butylcarbinols. (Mlle.) PAULINE LUCAS (*Compt. rend.*, 1911, 152, 1771—1774. Compare Abstr., 1910, i, 378).—A further examination of the hydrocarbons obtained previously by dehydrating the product of the action of an organo-magnesium halide on a trialkylacetophenone. The substance to which the formula $CMe_3\cdot CPh\colon CH_2$ was ascribed appears to be a mixture of a liquid having this constitution with 1-*phenyl*-2 : 2-*dimethyl*cyclo*propane*, since on oxidation with chromic acid it furnishes acetone, acetophenone, and trimethylacetophenone ; the latter ketone was characterised by its *semicarbazone*, m. p. 195°.

Magnesium ethyl iodide acts on trimethylacetophenone to give *γ-phenyl-ββ-dimethylpentan-γ-ol*, $CMe_3\cdot CEtPh\cdot OH$, b. p. 115—116°/15 mm. When this is boiled with formic acid, it yields a single hydrocarbon, *γ-phenyl-δδ-dimethyl-Δ^{β}-hexene*, $CMe_3\cdot CPh\colon CHMe$, b. p. 90—95°/12 mm., the constitution of which follows from the formation of carbon dioxide and trimethylacetophenone on oxidation.

The hydrocarbon from γδ-diphenyl-ββ-dimethylbutan-γ-ol similarly gives carbon dioxide, benzoic acid, trimethylacetophenone, and a *substance*, $C_{18}H_{20}O$, b. p. 195—200°/15 mm. It is, therefore, probably *αβ-diphenyl-γγ-dimethyl-Δ^{α}-butylene*, $CMe_3\cdot CPh\colon CHPh$. The unidentified product of oxidation appears not to contain a carbonyl group.

W. O. W.

Preparation of Hydroxybenzyl Alcohol, Hydroxybenzaldehyde, and Hydroxybenzoic Acids. FRITZ RASCHIG (D.R.-P. 233631).—When substituted phenols containing an acid radicle in place of the hydroxyl hydrogen are quantitatively chlorinated at a temperature of 150—180°, derivatives containing chlorine in the side-chain only are obtained.

*ω-Chloro-*o*-tolyl carbonate*, $CO(O\cdot C_6H_4\cdot CH_2Cl)_2$, m. p. 79°, prepared from *o*-tolyl carbonate, furnishes when boiled with calcium carbonate and water under 4—5 atmospheres pressure a satisfactory yield of *o*-hydroxybenzyl alcohol (saligenin).

*ω-Dichloro-*o*-tolyl carbonate*, $CO(O\cdot C_6H_4\cdot CHCl_2)_2$, m. p. 73°, b. p. 247°/30 mm., when similarly treated furnishes salicylaldehyde.

*ω-Dichloro-*p*-tolyl carbonate*, m. p. 108°, is decomposed into *p*-hydroxybenzaldehyde, whilst *ω-trichloro-m-tolyl carbonate*, $CO(O\cdot C_6H_4\cdot CCl_3)_2$, an unstable oil, yields *m*-hydroxybenzoic acid.

o-*Tolyl phosphate*, $PO(O\cdot C_6H_4Me)_3$, an oil, b. p. 410°/760 mm., prepared from *o*-cresol and phosphoryl chloride, yields *ω-dichloro-*o*-tolyl phosphate*, m. p. 78°, and subsequently salicylaldehyde.

o-*Tolyl phosphite*, $P(O\cdot C_6H_4Me)_3$, prepared from *o*-cresol and phosphorus trichloride on chlorination, yields first an additive product, $(CH_3\cdot C_6H_4O)_3PCl_2$, and subsequently a viscous oil consisting chiefly of

*ω-dichloro-*o*-tolyl dichlorophosphate*, $(CHCl_2\cdot C_6H_4\cdot O)_3PCl_2$, and on hydrolysis, salicylaldehyde.

o-Tolyl benzenesulphonate, $C_6H_4Me\cdot O\cdot SO_2Ph$, yields *ω-dichloro-*o*-tolyl benzenesulphonate*, needles, m. p. 73°, and salicylaldehyde on hydrolysis.

*ω-Dichloro-*m*-tolyl benzoate*, $OBz\cdot C_6H_4\cdot CHCl_2$, obtained from *m*-tolyl benzoate, is an unstable oil, which cannot be distilled even in a vacuum, and on hydrolysis yields a mixture of benzoic acid and *m*-hydroxybenzaldehyde. F. M. G. M.

Catalytic Esterification of Aromatic Acids in the Wet Way. JEAN B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1911, **152**, 1855—1857. Compare this vol., i, 600).—Contrary to what has been noticed in the case of the aliphatic acids, the extent and rapidity of the esterification of benzoic acid increases with the amount of sulphuric acid employed as a catalyst, but not with that of potassium hydrogen sulphate or hydrated aluminium sulphate, which only give poor yields of the ester. The same observation applies to salicylic acid and the toluic acids, but phenylacetic and phenylpropionic acids more closely resemble acetic acid in this respect. W. O. W.

Alkyl Chloro- and Bromo-anthranilates. PAUL FREÜNDLER (*Bull. Soc. chim.*, 1911, [iv], **9**, 605—608).—Methyl 5-chloroanthranilate (Abstr., 1907, i, 158) is readily obtained by direct chlorination by Flürscheim's method (Trans., 1908, **93**, 1772), using a mixture of acetic and hydrochloric acids as a solvent. A small amount of the 3 : 5-dichloro-ester is formed in the reaction, but this is easily separated owing to its insolubility in dilute hydrochloric acid. *Methyl* 3 : 5-*dichloroanthranilate*, m. p. 63—64°, crystallises in colourless needles, and is very soluble in alcohol.

The process used by Wheeler (Abstr., 1909, i, 382) for the bromination of anthranilic acid gives good results for the methyl ester. *Methyl* 5-*bromoanthranilate*, m. p. 74°, crystallises in yellowish-white prisms. The *dibromo*-ester (? 3 : 5) formed simultaneously has m. p. 84°, crystallises in slender needles, and is soluble in alcohol.

T. A. H.

Further Investigation of Certain Derivatives of *o*-Sulphobenzoic Acid. PHILIP H. COBB and GEORGE P. FULLER (*Amer. Chem. J.*, 1911, **45**, 605—611).—It has been shown by Cobb (Abstr., 1906, i, 499) that the substance, m. p. 162—163°, obtained by Remsen and Saunders (Abstr., 1895, i, 474) and List and Stein (Abstr., 1898, i, 584) by the action of benzene and aluminium chloride on a mixture of the chlorides of *o*-sulphobenzoic acid, is diphenylbenzylsulphone, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CPh_2}{SO_2-}}{>}O$, and can be prepared by the action of magnesium phenyl bromide on *o*-sulphobenzoic anhydride.

Sachs (Abstr., 1904, i, 877) has stated that when "methylsaccharin" is treated with magnesium phenyl bromide, triphenylcarbinol-*O*-sulphonmethylamide is produced, which, when heated with concentrated hydrochloric acid in a sealed tube at 150°, yields a com-

pound, m. p. 210°, which he regarded as diphenylbenzylsulphone. On repeating these experiments, it has been found that Sachs' compound (m. p. 210°) is not diphenylbenzylsulphone, but the *lactam*, $C_6H_4<\substack{CPh_2\\SO_2-}>NMe$, and that the same substance is produced when triphenylcarbinol-*O*-sulphonemethylamide is treated with concentrated sulphuric acid for twelve hours at 50°.

When *di*-p-*tolylphenylcarbinol*-O-*sulphonmethylamide*,

$$OH\cdot C(C_6H_4Me)_2\cdot C_6H_4\cdot SO_2\cdot NHMe,$$

m. p. 243° (uncorr.), obtained by the action of magnesium *p*-tolyl bromide on "methylsaccharin," is heated with concentrated hydrochloric acid for fourteen hours at 150°, or with concentrated sulphuric acid at 70°, no change takes place and the substance can be recovered.

E. G.

Ketens. XX. Attempts to Prepare Quinoketens. HERMANN STAUDINGER and KARL CLAR (*Ber.*, 1911, 44, 1623—1633).—An account of unsuccessful attempts to synthesise the following quinonoid ketens: (I) $CO{:}C_6H_4{:}CO$, (II) $CPh_2{:}C_6H_4{:}CO$,

(III) $CO{:}C_6H_4{:}C{:}C_6H_4{:}CO$.

Terephthaloyl bromide, prepared by the action of phosphorus pentabromide on the corresponding acid in the presence of phosphoryl bromide, crystallises from light petroleum in long, colourless needles, m. p. 85°. When heated with zinc in ethereal solution, it yields ethyl terephthalate; no evidence of the formation of dioxoquinodimethane (1) was obtained.

Diphenyl-*p*-tolylcarbinol is prepared most readily by the interaction of magnesium phenyl bromide and phenyl *p*-tolyl ketone (compare Bistrzycki and Gyr, Abstr., 1904, i, 315; Acree, *ibid.*, 409). It is converted by prolonged boiling with dilute nitric acid into triphenylcarbinol-*p*-carboxylic acid, m. p. 203—205° (compare Bistrzycki and Gyr, *loc. cit.*), which, on treatment with phosphorus pentachloride or thionyl chloride, yields *ω-chlorotriphenylmethane*-4-*carboxyl chloride*, $CPh_2Cl\cdot C_6H_4\cdot COCl$. The latter forms colourless crystals, m. p. 80—81°, is very stable towards water, and, when treated with aniline in ethereal solution, yields *ω-anilinotriphenylmethane*-4-*carboxylic acid*, $C_6H_5\cdot NH\cdot CPh_2\cdot C_6H_4\cdot CO_2H$, m. p. 182°.

Triphenylmethane-4-carboxylic acid, m. p. 165° (compare O. Fischer and Albert, Abstr., 1893, i, 196), obtained by reducing triphenylcarbinol-*p*-carboxylic acid with phosphorus and iodine in glacial acetic acid solution, is converted by thionyl chloride into the corresponding *chloride*, $CHPh_2\cdot C_6H_4\cdot COCl$, which forms white crystals, m. p. 89—90°; the *anilide*, $C_{26}H_{21}ON$, has m. p. 196°. All attempts to prepare diphenyloxoquinodimethane (II) either by the removal of hydrogen chloride from triphenylmethane-4-carboxyl chloride by means of quinoline and tripropylamine, or by the action of zinc on ω-chlorotriphenylmethane-4-carboxyl chloride, proved unsuccessful.

When an ethereal solution of the last-named compound is heated with zinc, or shaken with mercury in an atmosphere of carbon dioxide, an intense reddish-violet coloration, due to the formation of *triphenylmethyl*-4-*carboxyl chloride*, $-CPh_2\cdot C_6H_4\cdot COCl$, is produced. The violet

solution of the triphenylmethyl derivative is at once decolorised on exposure to air, or by the addition of bromine; when treated with aniline it yields *triphenylmethyl*-4-*carboxylanilide.*

The *peroxide*, $C_{40}H_{28}O_4Cl_2$, obtained by passing a stream of air through an ethereal solution of the chloride, crystallises in white plates, m. p. 168° (decomp.), and gives the usual peroxide reactions. It is decomposed by concentrated sulphuric acid, yielding triphenylcarbinol-*p*-carboxylic acid.

Methyl triphenylcarbinol-4-*carboxylate*, $C_{21}H_{18}O_3$, prepared by the action of methyl iodide on the corresponding silver salt, has m. p. 119°, and, on treatment with phosphorus pentachloride or oxalyl chloride, yields *methyl ω-chlorotriphenylmethane*-4-*carboxylate*, which forms a pale yellow, amorphous mass. When an ethereal solution of the chloro-ester is shaken with mercury, a reddish-violet solution of *methyl triphenylmethyl*-4-*carboxylate* is obtained.

The solution is stable towards water and aniline, but is decolorised on exposure to air, or by the addition of bromine. The *peroxide* forms a white powder, m. p. 171·5° (decomp.).

Benzophenone-4 : 4′-dicarboxylic acid is best prepared by heating di-*p*-tolyl ketone with dilute nitric acid and subsequently oxidising the monocarboxylic acid thus obtained with potassium permanganate in alkaline solution.

With phosphorus pentachloride it yields *di-ω-chlorodiphenylmethane*-4 : 4′-*dicarboxyl chloride*, $CCl_2(C_6H_4 \cdot COCl_2)_2$, which forms colourless crystals, m. p. 78°, and undergoes no change when heated with zinc in ethereal or ethyl acetate solution.

Benzophenone-4 : 4′-dicarboxylanilide, $C_{27}H_{20}O_3N$, has m. p. 302°.

F. B.

Action of Sunlight on *allo*-Cinnamic Acid. ANNE W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 100—101. Compare Riiber, Abstr., 1902, i, 785).—*allo*-Cinnamic acid (m. p. 41—42°) exposed to sunlight for some days became opaque and was no longer completely soluble in ether. The insoluble portion, dissolved in ammonia, gave a heavy precipitate with barium chloride. The acid from the barium salt melted at 206°, the m. p. being unchanged by mixing with β-truxillic acid from the coca-acids. The ether extract yielded, in addition, ordinary cinnamic acid, α-truxillic acid, and a trace of oil.

J. D. K.

Ketens. XXI. Attempts to Prepare Alleneketens. HERMANN STAUDINGER and E. OTT (*Ber.*, 1911, **44**, 1633—1637).—Attempts to synthesise allene-ketens of the type $CR_2:C:CO$ by the action of zinc on α-bromo-αβ-unsaturated acyl chlorides were unsuccessful.

α-Bromocinnamoyl bromide, obtained by the interaction of phosphorus pentabromide and the corresponding acid in benzene solution, has b. p. 170°/23 mm. The chloride is best prepared by the action of thionyl chloride on the acid (compare Anschütz and Selden, Abstr., 1887, 829); when heated with zinc in ethyl acetate solution, it yields

a brown, amorphous *substance*, m. p. 206°, which contains chlorine, but is free from bromine.

In the preparation of $\beta\beta$-dimethylacrylic acid from ethyl α-bromo*iso*valerate, the removal of hydrogen bromide is most readily effected by means of quinoline; the *chloride* has b. p. 145—150°; the *anilide*, m. p. 126—127°.

α-Bromo-$\beta\beta$-dimethylacrylic acid is obtained in almost quantitative yield by the action of alcoholic sodium ethoxide on $\alpha\beta$-dibromo*iso*valeric acid (compare Massot, Abstr., 1894, i, 356); on treatment with thionyl chloride, it yields the *chloride*, $CMe_2{:}CHBr{\cdot}COCl$, which has b. p. 178° or 73°/16 mm., and when heated in ethyl acetate solution with zinc gives brown, amorphous products; the *anilide*,

$$C_{11}H_{12}ONBr,$$

has m. p. 90°.

Benzylidenemalonyl chloride, prepared by the action of phosphorus pentachloride on the corresponding acid in the presence of light petroleum, crystallises in white needles, m. p. 37°. It yields with pyridine an *additive* compound, $C_{20}H_{16}O_2N_2Cl_2$, which forms a pale yellow powder, m. p. 95—100° (decomp.).

Attempts to prepare benzylidenemalonic anhydride by the action of silver oxide on the chloride in ethereal solution yielded ethyl benzylidenemalonate. F. B.

Addition of Hydrogen Cyanide to Unsaturated Compounds. PHILIP H. COBB (*Amer. Chem. J.*, 1911, **45**, 604—605).—During the course of some work on phenylmaleic and phenylfumaric acids, it was found that when an alcoholic solution of ethyl phenylpropiolate is treated with an aqueous solution of potassium cyanide and the mixture boiled for some hours on the water-bath, potassium carbonate and phenylsuccinonitrile are produced in accordance with the equation:

$$CPh{:}C{\cdot}CO_2Et + 2KCN + 2H_2O = CN{\cdot}CHPh{\cdot}CH_2{\cdot}CN + K_2CO_3 + EtOH.$$

This reaction is being extended to other unsaturated compounds.

E. G.

Esters of Boric Acid. GEORG COHN (*Pharm. Zentr.-h.*, 1911, **52**, 479—485).—Esters of boric acid can be readily prepared by treating the acid with an excess of the alcohol in presence of hydrogen chloride or of sulphuric acid. A large excess of alcohol (five or six times the weight of boric acid) gives the best yield, and sulphuric acid is preferable to hydrogen chloride. In this way the methyl, ethyl, propyl, and *iso*butyl esters have been prepared.

Attempts to employ these esters for the alkylation of bases, phenols, and acids were unsuccessful, except in the case of salicylic acid, which, when boiled for a long time with methyl borate, yielded methyl salicylate quantitatively. *p*-Hydroxybenzoic acid remains unchanged under these conditions, and no reaction was observed with aniline, dimethylaniline, phenol, or resorcinol.

Aromatic hydroxy-acids react readily with boric esters, yielding substances of the type of *trisalicylboric acid*, $B(O{\cdot}C_6H_4{\cdot}CO_2H)_3$, which

is formed initially in the above-mentioned esterification. The compound crystallises in long prisms, which on heating begin to sinter at about 230°, and are completely melted (with energetic decomp.) at 260—270°. When trisalicylboric acid is boiled with phenylhydrazine, a substance, m. p. 223°, is obtained, which crystallises in light brown laminæ, and reduces copper sulphate even in the cold. *m*- and *p*-Hydroxybenzoic acids do not give analogous compounds. *Tri-o-hydroxytoluoylboric acid* sinters at 220°, and has m. p. 245—247° (decomp.). *Tri-*m*-hydroxytoluoylboric acid* sinters at 175°, but melts sharply at 261° (decomp.). *Tri-*p*-hydroxytoluoylboric acid* sinters at 143°, and has m. p. 210—212° if slowly heated; if plunged into a bath at 155° the substance froths up, crystallises, and melts then at 210—212°.

Tri-α-hydroxynaphthoylboric acid sinters at 250°, m. p. 255° (decomp.). *Tri-β-hydroxynaphthoylboric acid* is still solid at 263°.

Triresorcinoylboric acid (from carefully dried resorcinic acid) becomes yellow at 220°, but suffers no further change below 260°.

Gallic acid does not react. Tartaric acid and methyl or ethyl borate yield a small quantity of a white, crystalline *substance*.

Salicylamide and boric ester yield a white, crystalline *substance*, which begins to sinter at 220°, and melts at about 265°. The analyses indicate the composition $B(O\cdot C_6H_4\cdot CO\cdot NH_2)_3$. R. V. S.

Ketens. XXII. Attempts to Prepare ω-Methoxyphenylketen. HERMANN STAUDINGER and OTTO KUPFER (*Ber.*, 1911, **44**, 1638—1640).—Attempts to remove hydrogen chloride from phenylmethoxyacetyl chloride by means of tripropylamine, with the formation of phenylmethoxyketen, proved fruitless.

ω-Methoxyphenylacetyl chloride, $OMe\cdot CHPh\cdot COCl$, prepared by the action of thionyl chloride on the corresponding acid, is a colourless liquid, b. p. 80—81°/0·1 mm. At temperatures above 120°, it decomposes into carbon monoxide, methyl chloride, and benzaldehyde.

F. B.

Ether Derivatives of β-Phenylhydracrylic Acid (β-Hydroxy-β-phenylpropionic Acid). WALTHER SCHRAUTH, WALTER SCHOELLER, and RICHARD STRUENSEE (*Ber.*, 1911, **44**, 1432—1436).—The anhydrides of α-hydroxymercuri-β-alkyloxy-β-phenylpropionic acids,

$$OR\cdot CHPh\cdot CH{<}{}^{CO}_{Hg}{>}O$$

(this vol., i, 595), when hydrolysed with mineral acids are completely decomposed, yielding cinnamic acids, and when the esters of the α-acetoxymercuri-β-alkyloxy-β-phenylpropionic acids are treated with an alcoholic solution of hydrogen sulphide, esters of cinnamic acid are formed. By using an alcoholic solution of ammonium sulphide the esters of the mercuriacetate derivatives can be transformed into esters of β-alkyloxy-β-phenylpropionic acids. The corresponding acids can be obtained by hydrolysing the esters or by the action of hydrogen sulphide on solutions of the anhydro-compounds in dilute sodium hydroxide.

Methyl β-methoxy-β-phenylpropionate, $OMe\cdot CHPh\cdot CH_2\cdot CO_2Me$, pre-

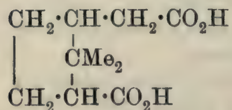
pared from the methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate, is an oil with b. p. 253° (corr.), and the corresponding *acid*, $C_{10}H_{12}O_3$, crystallises from light petroleum in stout, colourless plates, m. p. 98°.

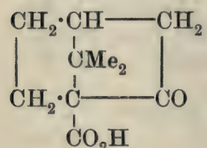
Methyl β-ethoxy-β-phenylpropionate, $OEt \cdot CHPh \cdot CH_2 \cdot CO_2Me$, is a colourless oil with an unpleasant odour, and has b. p. 256° (corr.). The corresponding *acid*, $C_{11}H_{14}O_3$, crystallises from light petroleum in colourless plates, m. p. 75°, and when boiled for a short time with hydrochloric acid yields cinnamic acid.

β-Propoxy-β-phenylpropionic acid, $OPr \cdot CHPh \cdot CH_2 \cdot CO_2H$, crystallises from water in colourless plates, m. p. 59°, and the corresponding iso*propoxy*-acid from light petroleum in plates, m. p. 73°. *β-iso-Butoxy-β-phenylpropionic acid*, $C_{13}H_{18}O_3$, has m. p. 67·5°. J. J. S.

Complete Synthesis of Pinophanic Acid and the Constitution of Ketopinic and Tricyclenic Acid.

GUSTAV KOMPPA (*Ber.*, 1911, **44**, 1536—1541).—The homo*apo*camphoric acid (annexed formula), prepared by reduction of *apo*camphoric anhydride to *apo*campholide, addition of potassium cyanide to this, and hydrolysis, is identical with pinophanic acid (Gilles and Rennwick, Proc., 1897, **13**, 65), but not with camphenecamphoric acid. Accordingly, ketopinic acid, from which pinophanic acid is obtained by heating with alkali or with sodium ethoxide, has the annexed formula, and not that suggested by Bredt and May. It follows, further, from this that tricyclenic [dehydrocamphenylic] acid has the constitution suggested by Semmler and by Komppa and Hintikka (Abstr., 1908, i, 852), which readily explains the conversion into ketopinic acid. The corresponding cyclic ketone has been obtained from homo*apo*camphoric acid in small quantities; the semicarbazone has m. p. 209—211°, and the ketone is probably identical with fenchocamphorone.





dl-apo*Campholide*, obtained by reducing *apo*camphoric anhydride, crystallises in long, indefinite, feathery masses or short, thick, triclinic prisms, m. p. 164°. When kept with hydrogen bromide in acetic acid, *bromo*apo*campholic acid*, $CH_2Br \cdot C_7H_{12} \cdot CO_2H$, is obtained, crystallising in aggregates of indefinite crystals, m. p. 139°.

*Cyano*apo*campholic acid*, prepared by heating *apo*campholide with potassium cyanide, forms short, many-faced, but indefinite crystals, m. p. 141·5—142° (corr.). On hydrolysis, homo*apo*camphoric acid is obtained in rhombic plates, m. p. 203—204°, in every way identical with pinophanic acid prepared from ketopinic acid. The *dianilide* crystallises in slender needles, m. p. 194—195°. E. F. A.

Action of Benzoyl Chloride and Potassium Cyanide on Benzoyloxybenzoic Acids and on Acylated Hydroxybenzoyloxybenzoic Acids.

FRANCIS E. FRANCIS and MAX NIERENSTEIN (*Annalen*, 1911, **382**, 194—210. Compare Francis and Davis, Trans., 1909, **95**, 1404; Davis, *ibid.*, 1910, **96**, 949).—By the action of

benzoyl chloride and potassium cyanide on hydroxybenzoyloxybenzoic acids, it was thought that acids of the type of galloylgallic acid (digallic acid), that is, compounds of the depside type (Fischer and Freudenberg, Abstr., 1910, i, 266), might be produced according to the equation: $OAc\cdot R\cdot CO\cdot O\cdot R'\cdot CO_2H + PhCO\cdot Cl + KCN =$

$$OAc\cdot R\cdot CO\cdot CN + PhCO\cdot O\cdot R'\cdot CO_2H + KCl.$$

The reaction takes place when the nucleus contains negative substituents, for example, 3-*m*-nitrobenzoyloxybenzoic acid, 4-*m*-nitrobenzoyloxybenzoic acid, 4-*m*-nitro-*p*-ethylcarbonatobenzoyloxybenzoic acid, diethylcarbonatoprotocatechuoyl-*o*-nitrosalicylic acid, 4-nitro-2-*p*-ethylcarbonatobenzoyloxybenzoic acid, and penta-acetylgalloylgallic acid, but not with the following acids: 4-benzoyloxybenzoic acid, 4-*p*-ethylcarbonatobenzoyloxybenzoic acid and the corresponding 3-oxy-acid, 4-*mp*-diethylcarbonatobenzoylbenzoic acid, and 3-nitro-4-dimethylcarbonatobenzoyloxybenzoic acid.

3-m-*Nitrobenzoyloxybenzoic acid*, $NO_2\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$, obtained by the action of *m*-nitrobenzoyl chloride on *m*-hydroxybenzoic acid at 40° in the presence of 10% sodium hydroxide solution, crystallises from dilute alcohol in stout needles, m. p. 241°. The isomeric 4-m-*nitrobenzoyloxybenzoic acid* crystallises from methyl alcohol in long needles, m. p. 273—274° (decomp.). When shaken with benzoyl chloride and an aqueous solution of potassium cyanide, the two acids yield respectively *m*-benzoyloxybenzoic acid and *p*-benzoyloxybenzoic acid together with *m*-nitrobenzoylformic acid (Claisen and Thompson, Abstr., 1880, 253).

3-*Nitro*-4-*ethylcarbonatobenzoic acid*, $CO_2Et\cdot O\cdot C_6H_3(NO_2)\cdot CO_2H$, prepared from 3-nitro-4-hydroxybenzoic acid, ethyl chlorocarbonate, and *N*-sodium hydroxide solution, crystallises from dilute alcohol in stellate masses of needles, m. p. 117°. The corresponding *acid chloride*,

$$CO_2Et\cdot O\cdot C_6H_3(NO_2)\cdot COCl,$$

crystallises from a mixture of chloroform and light petroleum in long needles, m. p. 72°, and condenses with *p*-hydroxybenzoic acid in the presence of alkali, yielding 3-*nitro*-4-p-*ethylcarbonatobenzoyloxybenzoic acid*, $CO_2Et\cdot O\cdot C_6H_3(NO_2)\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$, which crystallises from aqueous acetone in plates or from dilute alcohol in short, stout needles, m. p. 194—196° after beginning to sinter at 184°. Its decomposition into *m*-nitro-*p*-ethylcarbonatophenylglyoxylonitrile and *p*-benzoyloxybenzoic acid proceeds smoothly. The nitrile could not be isolated, but the crude oil when hydrolysed with concentrated hydrochloric acid gave 3-*nitro*-4-*hydroxyphenylglyoxylic acid*,

$$NO_2\cdot C_6H_3(OH)\cdot CO\cdot CO_2H,$$

which crystallises from chloroform in glistening prisms, m. p. 61° after sintering at 59°.

3 : 4-*Diethylcarbonatobenzoic acid*, $C_6H_3(O\cdot CO_2Et)_2\cdot CO_2H$, crystallises from dilute acetone in brilliant plates, m. p. 122—123° (decomp.); the corresponding *chloride*, $C_{13}H_{13}O_7Cl$, crystallises from a mixture of chloroform and light petroleum, has m. p. 55°, and reacts with *o*-nitrosalicylic acid in the presence of ether and dilute sodium hydroxide solution, yielding *nitro*-2-mp-*diethylcarbonatobenzoyloxybenzoic acid*, $C_6H_3(O\cdot CO_2Et)_2\cdot CO\cdot O\cdot C_6H_3(NO_2)\cdot CO_2H$, which crystallises from dliute alcohol in brilliant, glistening needles, m. p. 212—214°

(decomp.) when quickly heated. With benzoyl chloride and potassium cyanide solution it yields o-*nitro-2-benzoyloxybenzoic acid*,

$$OBz\cdot C_6H_4(NO_2)\cdot CO_2H,$$

m. p. 117°, and a nitrile which on hydrolysis gave 3 : 4-*dihydroxyphenylglyoxylic acid*, $C_6H_3(OH)_2\cdot CO\cdot CO_2H$. This acid crystallises from a mixture of chloroform and light petroleum in needles, m. p. 92°.

3 : 4-*Diethylcarbonatophenylglyoxylonitrile*, $C_6H_3(O\cdot CO_2Et)_2\cdot CO\cdot CN$, prepared from an ethereal solution of the corresponding chloride and an aqueous solution of potassium cyanide, crystallises from light petroleum in glistening needles, m. p. 38°. 4-*Nitro*-2-p-*ethylcarbonatobenzoyloxybenzoic acid*, $CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_3(NO_2)\cdot CO_2H$, crystallises in small prisms, m. p. 194—196° (decomp.), and with benzyl chloride and potassium cyanide yields p-*ethylcarbonatophenylglyoxylonitrile*, $CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot CN$, as small needles, m. p. 34°, and volatile under 10—12 mm. pressure. The nitrile when hydrolysed with concentrated hydrochloric acid yields p-*hydroxyphenylglyoxylic acid*, $OH\cdot C_6H_4\cdot CO\cdot CO_2H$, which crystallises from benzene in small cubes, m. p. 84°.

Penta-acetylgalloylgallic acid (Abstr., 1909, i, 402) reacts with benzoyl chloride and potassium cyanide, yielding 5-*benzoyl*-3 : 4-*diacetylgallic acid*, $C_6H_2(O\cdot COPh)(OAc)_2\cdot CO_2H$, which crystallises from methyl alcohol in small, pointed needles, m. p. 178—179°. The nitrile which was also formed when hydrolysed with concentrated hydrochloric acid gave *galloylformic acid*, $C_6H_2(OH)_3\cdot CO\cdot CO_2H$, which crystallises from dilute alcohol in glistening needles, m. p. 114—116°. It gives the same coloration with ferric chloride as does gallic acid, but with potassium cyanide solution it gives a violet coloration.

3 : 4 : 5-*Triethylcarbonatophenylglyoxylonitrile*,

$$C_6H_2(O\cdot CO_2Et)_3\cdot CO\cdot CN,$$

obtained from the corresponding chloride, crystallises from light petroleum in small, glistening needles, m. p. 98°.

3-p-*Ethylcarbonatobenzoyloxybenzoic acid*,

$$CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

crystallises from dilute acetone in colourless needles, m. p. 148°, and 3-*nitro*-4-*dimethylcarbonatobenzoyloxybenzoic acid*,

$$(CO_2Me\cdot O)_2C_6H_3\cdot CO\cdot O\cdot C_6H_3(NO_2)\cdot CO_2H,$$

prepared from 2 : 4-dimethylcarbonatobenzoyl chloride (Fischer, Abstr., 1909, i, 162) and *m*-nitro-*p*-hydroxybenzoic acid, crystallises from alcohol in small needles, m. p. 172° (decomp.). J. J. S.

Compounds of the Propane Series. SIEGMUND GABRIEL (*Ber.*, 1911, **44**, 1905—1915. Compare Hildesheimer, Abstr., 1910, i, 891). —Hildesheimer (*loc. cit.*) has described the compound obtained by the action of red phosphorus and bromine on α-phthaliminobutyric acid as αβ-dibromo-α-phthaliminopropane. A compound of this constitution has now been prepared independently, and found not to be identical with Hildesheimer's compound, which, accordingly, must have the composition of an αγ-dibromo-α-phthaliminopropane,

$$C_8H_4O_2{:}N\cdot CHBr\cdot CH_2\cdot CH_2Br.$$

By the action of bromine on phthaliminoacetone, mono-, di-, tri-, and tetra-bromo-derivatives have been obtained.

Phthaliminobromoacetone, $C_8H_4O_2{:}N{\cdot}CH_2{\cdot}CO{\cdot}CH_2Br$, prepared either by the action of phosphorus pentabromide or of bromine in chloroform solution on phthaliminoacetone, crystallises in colourless, slender, matted needles, m. p. 147—148°. When fused with potassium phthalimide, diphthaliminoacetone is obtained, proving the position of the bromine atom, whilst on heating with sodium acetate at 170°, *phthaliminohydroxyacetone*, crystallising in needles of silky lustre, m. p. 141—142°, is formed.

On hydrolysis of phthaliminobromoacetone by boiling with water, phthalimide and methylglyoxal are the main products.

Phthaliminodibromoacetone, $C_8H_4O_2{:}N{\cdot}CHBr{\cdot}CO{\cdot}CH_2Br$, produced on bromination in benzene solution or further bromination of the monobromo-compound, forms long needles, m. p. 126—127°. On hydrolysis, phthalimide and bromomethylglyoxal are obtained.

Phthaliminotribromoacetone, $C_8H_4O_2{:}N{\cdot}CHBr{\cdot}CO{\cdot}CHBr_2$, crystallises in obliquely-cut rods, m. p. 146—147°. On hydrolysis phthalimide and dibromomethylglyoxal are obtained, the latter being identified as the phenylhydrazone, crystalling in citron-yellow needles, m. p. 174°—175°.

Phthaliminotetrabromoacetone, $C_8H_4O_2{:}N{\cdot}CHBr{\cdot}CO{\cdot}CBr_3$, crystallises in rhombic plates, m. p. 153—154°. On hydrolysis bromoform is obtained.

On distillation of phthalimino-*n*-butyryl chloride, propenylphthalimide, m. p. 151°, is obtained (compare Johnson and Jones, this vol., i, 455). The isomeric *phthaliminocyclopropane*, $C_8H_4O_2{:}N{\cdot}CH{<}{\begin{array}{l}CH_2\\ |\\ CH_2\end{array}}$, prepared from amino*cyclo*propane and phthalic acid, forms colourless, rhombic plates, m. p. 135—136°. It does not form an additive compound with bromine.

Propenylphthalimide combines with bromine in chloroform solution, forming *phthalimino-αβ-dibromopropane*, $C_8H_4O_2{:}N{\cdot}CHBr{\cdot}CHBr{\cdot}CH_3$, which crystallises in flat, hexagonal crystals, m. p. 105—106°, and differs from Hildesheimer's compound (*loc. cit.*), m. p. 147°. On hydrolysis, phthalimide and acetylcarbinol are obtained. E. F. A.

Composition of Phthalein Salts. Richard Meyer and Ferd. Posner (*Ber.*, 1911, 44, 1954—1957).—The authors have carefully re-investigated the composition of the red sodium salt of phenolphthalein and the violet sodium salt of hydroquinonephthalein, and obtain results which are in agreement with the formulæ :

$$CO_2Na{\cdot}C_6H_4{\cdot}C{<}{\begin{array}{l}C_6H_4{\cdot}ONa\\ C_6H_4{:}O\end{array}} \quad \text{and} \quad CO_2Na{\cdot}C_6H_4{\cdot}C{\begin{array}{c}C_6H_3{\cdot}ONa\\ \diamond\ O\\ C_6H_3{:}O\end{array}}$$

previously assigned to these compounds (Meyer and Spengler, Abstr., 1905, i, 440; compare Baeyer, Abstr., 1910, i, 249; Kehrmann, *ibid.*, 406).

The calcium salt of phenolphthalein is obtained crystalline by shaking phenolphthalein with water and calcium hydroxide at the ordinary temperature, and heating the resulting solution to boiling. It has the composition $C_{20}H_{12}O_4Ca,1\frac{1}{2}H_2O$, and forms reddish-brown, flat

prisms with a green lustre; the anhydrous salt has a metallic-green colour (compare D.R.-P. 223969). F. B.

By-products of the Preparation of Ethyl Phloroglucinol-dicarboxylate. HERMANN LEUCHS and FRITZ SIMION (*Ber.*, 1911, **44**, 1874—1884. Compare Leuchs and Geserick, Abstr., 1909, i, 106).—In the preparation of ethyl phloroglucinol dicarboxylate by the Baeyer synthesis, ethyl malonate and ethyl acetate are present in the reaction mixture, and there is the possibility of 3 mols. of acetate uniting to form phloroglucinol, or of 3 mols. of malonate uniting to form a tricarboxylate, or of the formation of phloroglucinolmonocarboxylate from 2 mols. of acetate and 1 mol. of malonate. The by-products of the reaction have been examined from this point of view, and five such isolated, namely, an *ester*, $C_{17}H_{20}O_{10}$, m. p. 96°, an *acid*, $C_{15}H_{16}O_{10}$, and an *ester*, $C_{14}H_{16}O_8$, both derived from this by secondary changes, a compound, $C_{22}H_{20}O_{12}$, and a compound, $C_{18}H_{18}O_{11}$, formed by the combination of 4 mols. of ethyl malonate.

Neither phloroglucinol-mono- nor -tri-carboxylate is formed, although the latter may represent an intermediate stage in the formation of some of the compounds mentioned. More probably the molecules are first united in chains, and the closing of the ring takes place subsequently.

The *ester*, $C_{17}H_{20}O_{10}$, has been more fully investigated. With hydroxylamine, an *iso*oxazolone, $\begin{matrix} N\text{———}O \\ \| \\ CR\cdot CH_2 \end{matrix}\!\!>\!CO$, is formed. With concentrated nitric acid, the side-chain is hydrolysed, and the ester, $C_{14}H_{16}O_8$, formed.

On acetylation, a *triacetate* is formed, water being at the same time eliminated. On complete hydrolysis with hydrogen iodide, an *acid*, $C_9H_6O_5$, is obtained. Cold sodium hydroxide eliminates a molecule of alcohol.

The formula attached is applied to the ester $C_{17}H_{20}O_{10}$ to express this behaviour: $CO_2Et\cdot CH{<}\begin{matrix} CO\text{————}CH(CO_2Et) \\ CO\cdot CH(CO\cdot CH_2\cdot CO_2Et) \end{matrix}{>}CO$.

It crystallises in long, matted, colourless needles, m. p. 95·5—96·5°, and shows a deep reddish-brown coloration with ferric chloride.

The iso*oxazolone*, $C_{15}H_{15}O_9N$, produced on boiling with hydroxylamine, forms four-sided, glistening tablets or prisms, m. p. 203—204° (decomp.).

The *acetate*, $C_{23}H_{24}O_{12}$, crystallises in yellow, dome-like prisms, m. p. 109—110°. The mother liquors contain the *sodium* salt, four-sided, yellow plates, m. p. 260° (decomp.), of an *ester*, $C_{21}H_{20}O_{12}$ or $C_{19}H_{18}O_{11}$, which crystallises in needles, m. p. 145—146°. By the action of hydrogen iodide on the acetate, an *acid*, $C_9H_6O_3$, crystallising in feathery needles, is obtained, m. p. above 300°.

The *anhydride*, $C_{17}H_{18}O_9$, of the ester, $C_{17}H_{20}O_{10}$, crystallises in long, hexagonal needles, m. p. 153—154°.

With the ester, sodium hydroxide gives a product, $C_{15}H_{14}O_9$, crystallising in massive prisms, m. p. 162—163°.

Concentrated nitric acid forms from the ester, glistening, broad needles, m. p. 128—129°, of the *compound*, $C_{14}H_{16}O_8$, identical with

that formed during the original condensation. A second *product*, $C_{16}H_{18}O_{10}$, crystallises in needles or prisms, m. p. 99—100°.

The *condensation product*, $C_{15}H_{16}O_{10}$, consists of colourless, glistening, obliquely-cut prisms, m. p. 165° (decomp.). When fused, it forms the compound, $C_{14}H_{16}O_{8}$, just described.

The by-product, $C_{22}H_{20}O_{12}$, forms pale yellow needles, m. p. 196—197°.

The fifth condensation product, the ester, $C_{18}H_{18}O_{11}$, crystallises in yellow, pointed, four-sided plates, m. p. 177—178°, and is identical with a substance isolated by Willstätter (Abstr., 1899, i, 577). It yields phloroglucinol when fused with potassium hydroxide, and is considered to be formed by the condensation of 4 mols. of ethyl malonate. E. F. A.

Synthesis of Glucovanillic Acid and of Gluco-*p*-hydroxybenzoic Acid. FERDINAND MAUTHNER (*J. pr. Chem.*, 1911, [ii], 83, 556—560. Compare Abstr., 1910, i, 677).—*Methyl tetra-acetylglucovanillate*, $C_{23}H_{28}O_{13}$, m. p. 144—145°, obtained by shaking a solution of methyl vanillate in dilute sodium hydroxide with ethereal β-acetobromoglucose for twenty-six hours, is hydrolysed by aqueous barium hydroxide at the ordinary temperature, yielding Tiemann and Reimer's glucovanillic acid.

In a similar manner, methyl *p*-hydroxybenzoate and β-acetobromoglucose yield *methyl tetra-acetylgluco-*p*-hydroxybenzoate*, $C_{22}H_{26}O_{12}$, m. p. 159—160°, which is converted into *gluco-*p*-hydroxybenzoic acid*, $C_{13}H_{16}O_{8}$, m. p. 211—212°, by shaking with 6% barium hydroxide for twenty-four hours at the ordinary temperature. C. S.

Chemical Action of Light. XXI. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1911, **44**, 1558—1564).—By the action of light on benzaldehyde a *trimeride*, m. p. 144—145°, is obtained, isomeric with that of Mascarelli, m. p. 247—248°, which is also formed in this reaction. The new polymeride crystallises in chalk-white, microcrystalline crusts, and does not combine with semicarbazide. Cinnamaldehyde after a year's exposure to light gives a reddish-brown, transparent resin, which after purification forms an almost colourless powder, m. p. 115°; this is probably a *polymeride* of four or five molecules.

A mixture of benzophenone and benzaldehyde when exposed to light forms a *compound*, $C_{27}H_{22}O_{3}$, composed of two molecules of benzaldehyde and one of benzophenone. This crystallises in colourless, voluminous needles, m. p. 245°.

A mixture of benzophenone and diethyl dihydrocollidinedicarboxylate in benzene yields after a year's exposure a mixture of benzopinacone and ethyl collidinedicarboxylate. The *picrate* of the latter forms large, yellow needles, m. p. 164°; the *aurichloride* is oily, and the *platinichloride* yields orange-red platelets, m. p. 181°.

Quinaldine and acetone unite to a condensation product, $C_{23}H_{22}N_{2}$, composed of 2 mols. of quinaldine and 1 mol. of acetone, which crystallises in light yellow, slender needles, m. p. 212°. It is a diacid base; on the addition of hydrochloric acid it becomes orange-red, but on stirring

the solution becomes colourless. When this is evaporated a barely yellow-coloured residue is obtained, which immediately becomes orange-red on the addition of water.

The *dihydrochloride* is colourless; the *monohydrochloride* is orange-red, m. p. 270°. The *platinichloride* is orange-red; the *aurichloride* is at first a golden-yellow, crystalline precipitate, but with water a brown mass is obtained and the filtrate is violet-brown. E. F. A.

Rate of Transformation of *syn-* into *anti-*Oximes. THOMAS S. PATTERSON and ANDREW McMILLAN (*Proc. Phil. Soc. Glasgow*, 1911, Reprint 7 pp.).—In continuation of previous work (Trans., 1907, **91**, 504; 1908, **93**, 1042), the authors have determined the velocity of transformation of a number of substituted benz*syn*aldoximes into the *anti*-forms in ethyl tartrate solution.

The following are the mean values for 1000 k at 26°: Benz*syn*-aldoxime, 6·38; *p*-tolyl*syn*aldoxime, 5·18; anis*syn*aldoxime, 6·82; piperonal*syn*aldoxime, 3·59; *o*-nitrobenz*syn*aldoxime, 1·10; *m*-nitrobenz*syn*aldoxime, 4·16; *p*-iodobenz*syn*aldoxime, 5·335.

In the case of *p*-nitrobenz*syn*aldoxime the transformation into the *anti*-oxime takes place so rapidly that no measurements of the rate of change could be made. F. B.

Synthesis of α-Amino-ketones by means of Hexamethylenetetramine. CARL MANNICH and FRIEDRICH L. HAHN (*Ber.*, 1911, **44**, 1542—1552).—A large number of α-halogen ketones readily form crystalline additive products with hexamethylenetetramine, iodides reacting more readily than bromides or chlorides. These compounds are colourless, soluble salts, which tend to decompose when crystallised and decompose also on warming. When hydrolysed with a large excess of alcohol and 38% hydrochloric acid, the corresponding amines are obtained, but the reaction is complicated by the formation of condensation products with the formaldehyde derived from hexamethylenetetramine. In the case of those bases which are stable in the free state, the formaldehyde can be fixed by adding sodium hydrogen sulphite.

Two of the amino-ketones, ω-amino-*p*-hydroxyacetophenone,

$$OH\cdot C_6H_4\cdot CO\cdot CH_2\cdot NH_2,$$

and aminoacetylcatechol, $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot NH_2$, were obtained as free bases, although α-amino-ketones usually condense to form dihydropyrazines. The condensation is possibly hindered by the phenolic nature of the compounds, or more probably it depends on the solubility of the amino-ketones. When they are sparingly soluble, condensation does not take place.

ω-Chloroacetophenone and hexamethylenetetramine form a salt-like additive product, m. p. 145°. The similar compound from ω-bromoacetophenone and hexamethylenetetramine has m. p. 165°. Either product on treatment for three days with hydrochloric acid and alcohol gives the *hydrochloride* of *aminoacetophenone*, m. p. 186—187°; the *hydrobromide* has m. p. 217—218° (decomp.).

ω-Carbethoxyaminoacetophenone, $C_6H_5\cdot CO\cdot CH_2\cdot NH\cdot CO_2Et$, prepared by the interaction of the aminoacetophenone salts with ethyl chloro-

carboxylate, crystallises in slender needles, m. p. 58°. It is reduced by sodium amalgam and alcohol to *ω-carbethoxyaminomethylphenylcarbinol*, which crystallises in colourless plates, m. p. 86°.

ω-Chloro-*p*-methoxyacetophenone and hexamethylenetetramine condense to a product, m. p. 170°, which is decomposed into *ω-amino-*p*-methoxyacetophenone hydrochloride*, m. p. 197° (decomp.); this becomes red in solution on the addition of ammonia, and orange needles of a dihydropyrazine separate.

*ω-Amino-*p*-hydroxyacetophenone hydrochloride* crystallises in colourless platelets, m. p. 242° (decomp.). The free *base* is stable, crystallising in glistening plates.

Ethyl carbonato-ω-carbethoxyaminoacetophenone,

$$CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot CH_2\cdot NH\cdot CO_2Et,$$

forms slender, colourless plates, m. p. 85—86°.

ω-Chloroacetylcatechol, m. p. 173°, is best prepared by heating equal quantities of catechol, chloroacetic acid, and phosphoryl chloride in a large flask on the water-bath until the liberation of hydrogen chloride ceases. The *diacetate* has m. p. 110—111°, but the additive product with hexamethylenetetramine could not be obtained pure.

ω-Iodoacetylcatechol diacetate, obtained by interaction of the chloride with sodium iodide, has m. p. 110—111°; it forms a hexamethylenetetramine *additive product*, m. p. 171°.

ω-Aminoacetylcatechol is a heavy powder, decomp. above 200°; the hydrochloride crystallises in lustrous plates, which become brown at 230°, m. p. 252° to a dark red liquid.

ω-Bromoacetoveratrone, $C_6H_3(OMe)_2\cdot CO\cdot CH_2Br$, obtained by bromination of acetoveratrone in chloroform, has m. p. 80—81°; the *additive product* with hexamethylenetetramine crystallises in needles.

ω-Aminoacetoveratrone hydrochloride forms colourless, lustrous needles, m. p. 221°.

ω-Chloroacetylpyrogallol triacetate, $C_6H_2(OAc)_3\cdot CO\cdot CH_2Cl$, has m. p. 100—101°. When oxidised with potassium permanganate in acetone, an acid containing acetyl is obtained, which is hydrolysed to pyrogallolcarboxylic acid, thus proving the positions 1, 2, 3, 4 for the substituting groups in chloroacetylpyrogallol. The triacetate does not combine with hexamethylenetetramine.

ω-Iodoacetylpyrogallol triacetate has m. p. 139—140°; it forms an additive product with hexamethylenetetramine, m. p. 130°, but ω-aminoacetylpyrogallol could not be obtained from this.

Acetylpyrogallol trimethyl ether has b. p. 165°/12 mm., m. p. 14—15°. *Bromoacetylpyrogallol trimethyl ether* is a viscid oil, m. p. 174—176°, forming colourless crystals, m. p. 50—51°; it does not form a hexamethylenetetramine additive compound. E. F. A.

Isolation of an Enolic Dibromide and the Course of the Reaction in the Bromination of Acetophenone and Similar Ketones. FRIEDRICH L. HAHN (*Ber.*, 1911, 44, 1552—1553).—When bromine is passed into a well cooled solution of acetoveratrone in a little chloroform or ether, a yellowish-red *dibromide*, $C_{10}H_{12}O_3Br_2$, separates. This is very unstable, and decomposes completely within

twelve hours. When covered with ether and well shaken with dilute sodium hydroxide, both layers remain colourless; the ether on evaporation yields ω-bromoacetoveratrone, an indication that the ketone reacts in the enolic form, and that the dibromide has the formula $C_6H_3(OMe)_2{\cdot}CBr(OH){\cdot}CH_2Br$.

When acetophenone is brominated in ice-cold chloroform solution, no hydrogen bromide is liberated, neither does the brownish-red solution contain free bromine until at least 1 mol. of bromine for each mol. of ketone has been added. Only on warming or shaking with water is hydrogen bromide liberated, and the solution becomes lighter in colour; it then contains ω-bromoacetophenone. If bromination is performed in a solution of sodium acetate in acetic acid, bromine is not fixed, even at the temperature of the water-bath, so long as no enol is present. On the addition of concentrated hydrochloric acid a trace of enol is formed and a violent reaction sets in, the solution being immediately decolorised. E. F. A.

Chemical Action of Light. XX. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1911, **44**, 1554—1558. Compare *ibid.*, 1901, **34**, 1541).—By the action of light on a mixture of acetone (1 vol.) and ethyl ether (2 vols.) there are formed *iso*propyl alcohol, an additive product of acetone and ether, $C_7H_{16}O_2$, b. p. 138—141°, probably the *monoethyl ether* of *β-methylbutylene βγ-glycol*, and a product, $C_{11}H_{22}O_3$ or $C_{11}H_{24}O_3$, b. p. 109—112°/20 mm.

Acetophenone and ethyl ether after seven months' exposure to light yield an additive product, $C_{12}H_{18}O_2$, b. p. 247°, together with a further condensation product.

Benzophenone and ethyl ether form benzopinacone and an additive product, $C_{17}H_{20}O_2$, crystallising in colourless prisms, m. p. 51°, and stable towards permanganate; it has probably the composition $OH{\cdot}CPh_2{\cdot}CHMe{\cdot}OEt$. A more complicated condensation product is also obtained. E. F. A.

Ketens. XIX. Formation and Preparation of Diphenylketen. HERMANN STAUDINGER (*Ber.*, 1911, **44**, 1619—1623).—Diphenylketen is formed in almost quantitative yield by the interaction of equal molecular quantities of diphenylacetyl chloride and tripropylamine in ethereal solution. It is also obtained, together with ω-chlorodiphenylmethane and tetraphenylethylene, when diphenylacetyl chloride is distilled in a current of carbon monoxide under ordinary pressure. It is, however, best prepared by allowing a benzene solution of azibenzil to flow slowly into a flask heated at 100°, and distilling the resulting diphenylketen under diminished pressure (compare Schroeter, Abstr., 1909, i, 617).

The residue from the distillation separates from glacial acetic acid in yellow crystals of the composition $C_{28}H_{20}O_2N_2$, m. p. 201°, and consists of an *additive* compound of diphenylketen with azibenzil.

F. B.

Beckmann Transformation. FERDINAND HENRICH (*Ber.*, 1911, 44, 1533—1536. Compare Schroeter, this vol., i, 505).—When

ethereal solutions of the *syn*-modifications of dypnoneoxime (Abstr., 1904, i, 431) and of benzylideneacetophenoneoxime (Abstr., 1907, i, 324) are subjected to the Beckmann transformation by phosphorus pentachloride, white substances are first precipitated, which are then converted by the further addition of phosphorus pentachloride into the yellow products, from which the anilides are finally obtained by the action of water. Similar behaviour is exhibited by pivalophenoneoxime (Schroeter, *loc. cit.*) and by benzophenoneoxime. These white substances are shown to be the *hydrochlorides* of the oximes, since they are produced by passing hydrogen chloride into ethereal solutions of the *syn*-oximes, and regenerate the oximes by treatment with cold aqueous sodium carbonate. It seems, therefore, that an oxime undergoes the Beckmann transformation only when it has basic (unsaturated) properties. The *anti*-oximes of the preceding substances, which do not undergo the Beckmann transformation, likewise do not have pronounced basic (unsaturated) properties. C. S.

Isomerism and Isomorphism of the Yellow and the Red Fluorenones. Hans Stobbe (*Ber.*, 1911, **44**, 1481—1488).—Kerp's statement that the red and the yellow modifications of fluorenone (diphenylene ketone) are true isomerides (Abstr., 1896, i, 238) is confirmed by the author, who shows that the two substances differ, not only in the solid, but also in the liquid state and in solution.

The yellow ketone has m. p. 83—84°, and melts again at this temperature after resolidifying. The red ketone has m. p. 82—83°, but after resolidifying has m. p. 83—84°. Mixtures of the two ketones in any proportions have m. p. 83—84°. The fused mixture is orange, and solidifies in orange crystals. The red and the yellow, crystalline forms and also the orange mixed crystals are all isomorphous, crystallising in rhombic plates, more rarely in flattened needles. The red ketone crystallises from light petroleum in the dark, at first in blood-red, short crystals, but after repeated crystallisation in orange crystals which get paler in colour and more elongated, indicating a gradual conversion of the red into the yellow form. The conversion is readily accomplished by cold concentrated sulphuric acid.

The absorption spectra of the two modifications in alcohol, both in the visible and in the ultra-violet regions, have been measured. The latter are identical, the former, of course, are different. The optical behaviour leads the author to the opinion that Kerp's constitutions for the two ketones (*loc. cit.*) are untenable, and that the two substances furnish yet another instance of a pair of isomerides, the constitutions of which cannot be represented by present-day structural or stereochemical theories (compare Schaum, Abstr., 1910, i, 391).

C. S.

$\beta\zeta$-Dibenzoyl-$\beta\zeta$-dimethylheptane and $\alpha\alpha\epsilon\epsilon$-Tetramethylpimelic Acid. Albin Haller and Édouard Bauer (*Compt. rend.*, 1911, **152**, 1638—1642).—The general method for preparing trialkyl derivatives of acetic acid (Abstr., 1909, i, 131) has been applied to the synthesis of dibasic acids.

The sodium derivative of phenyl *iso*propyl ketone, prepared by

means of sodamide, reacts with $\alpha\gamma$-dibromopropane, giving a small quantity of an unstable liquid, b. p. 171—173°/13 mm., probably of the constitution $COPh\cdot CMe_2\cdot[CH_2]_2\cdot CH_2Br$; the principal portion of the product, however, consists of *$\beta\zeta$-dibenzoyl-$\beta\zeta$-dimethylheptane*,

$$COPh\cdot CMe_2\cdot[CH_2]_3\cdot CMe_2\cdot COPh,$$

silky needles, m. p. 48—49°, b. p. 250—255°/15 mm. This diketone forms a *dioxime*, m. p. 223—224°, and undergoes the usual scission when treated with sodamide, giving rise to *$\alpha\alpha\epsilon\epsilon$-tetramethylpimelamide*, needles, m. p. 191—192°. *$\alpha\alpha\epsilon\epsilon$-Tetramethylpimelic acid*,

$$CO_2H\cdot CMe_2\cdot[CH_2]_3\cdot CMe_2\cdot CO_2H,$$

forms hard crystals, m. p. 168—169°.

The reaction follows the same course when α-chloro-γ-bromopropane is used instead of the dibromo-derivative. *ϵ-Chloro-β-benzoyl-β-methylpentane*, $COPh\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2Cl$, has b. p. 165°/11 mm.

W. O. W.

o-Dibenzoylbenzene and its Homologues. ALFRED GUYOT and F. VALLETTE (*Ann. Chim. Phys.*, 1911, [viii], 23, 363—397).—Guyot and Catel (Abstr., 1905, i, 226, 516, 540; 1906, i, 761; 1907, i, 76) have drawn attention to the analogy which exists between the reactions of *o*-dibenzoylbenzene and those of diphenylphthalide and phenyloxanthranol, and Haller, Guyot, and Pignet have shown that under certain conditions the phthaleins are capable of being isomerised into *o*-dibenzoylbenzene derivatives (Abstr., 1910, i, 285). The authors have therefore generalised the work of Guyot and Catel, and prepared a number of dibenzoylbenzene homologues.

When magnesium phenyl bromide in ether reacts with excess of tolylphthalide, *2-hydroxy-2-phenyl-1-tolyl-1:2-dihydro*iso*benzofuran*, $C_6H_4<\begin{matrix}CH(C_6H_4Me)\\CPh(OH)\end{matrix}>O$, is formed. It is a colourless, crystalline powder, is very soluble in most organic solvents, and undergoes dehydration slowly at atmospheric temperature, but immediately and quantitatively on adding hydrochloric acid to its solution in alcohol, forming *2-phenyl-1-tolyl*iso*benzofuran*, $C_6H_4\lessdot\begin{matrix}C(C_6H_4Me)\\CPh\end{matrix}>O$, m. p. 83°, which crystallises in slender, yellow needles, gives yellow solutions showing a green fluorescence, of which the colour gradually disappears by the oxidation of the substance in air to *o-toluoylbenzoylbenzene*, m. p. 139°. This crystallises from a hot mixture of alcohol and benzene in small, brilliant prisms, dissolves in sulphuric acid with an intense magenta colour, and is recovered unchanged on addition of water. With hydrazine hydrate, it furnishes *phenyltolylphthalazine*, $C_6H_4<\begin{matrix}CPh\text{——}N\\C(C_6H_4Me)\cdot N\end{matrix}$, m. p. 117°, crystallising in small, colourless spangles. *o-Benzhydryltolhydrylbenzene*,

$$OH\cdot CHPh\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4Me,$$

m. p. 104°, is obtained by the reduction of either hydroxyphenyltolyldihydro*iso*benzofuran or benzoyltoluoylbenzene with sodium amalgam in alcohol. It crystallises in thin, colourless spangles. Under similar conditions, phenyltolyl*iso*benzofuran furnishes the *1:2-dihydride*, m. p. 104°, which crystallises in brilliant, colourless needles.

When, on the contrary, excess of magnesium phenyl bromide in ether is added to tolylphthalide, the condensation goes a stage further, and o-*tolhydryltriphenylcarbinol*, $HO\cdot CPh_2\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4Me$, m. p. 182°, small crystals, is formed. This, on treatment with warm sulphuric acid, loses 2 mols. of water and gives 10-*phenyl*-9-*tolylanthracene*, m. p. 192°, which crystallises in feebly yellow, bulky prisms, and fluoresces violet on solution in benzene. On oxidation with sodium dichromate, it yields 9 : 10-*dihydroxy*-10-*phenyl*-9-*tolyldihydroanthracene*, m. p. 212° (anhydrous), which crystallises with some alcohol in transparent needles, gives an indigo-blue coloration with sulphuric acid, and liberates iodine from potassium iodide. Its constitution is established by its synthesis from the ethyl ether of phenyloxanthranol by the action of magnesium tolyl bromide (compare Guyot and Staehling, Abstr., 1905, i, 885). In acetic acid solution, *o*-tolhydryltriphenylcarbinol is dehydrated by hydrochloric acid, forming 2 : 2-*diphenyl*-1-*tolyldihydro*iso*benzofuran*,

$$C_6H_4<\begin{matrix}\overset{*}{C}H(C_6H_4Me)\\ CPh_2\end{matrix}>O,$$

m. p. 123°, which crystallises in small, colourless needles from alcohol, and on oxidation with sodium dichromate in acetic acid exchanges the $\overset{*}{H}$ atom for a hydroxyl group; this *hydroxy*-compound has m. p. 130°, and crystallises from alcohol, ether, or benzene. Its constitution was established by its synthesis from diphenylphthalide by the action of magnesium tolyl bromide.

The action of magnesium *p*-tolyl bromide on tolylphthalide is analogous to that of magnesium phenyl bromide on this substance, and the following products were obtained by methods strictly analogous to those employed for the lower homologues described above.

2-*Hydroxy*-1 : 2-*ditolyl*-1 : 2-*dihydro*iso*benzofuran* forms small crystals, and on heating loses 1 mol. of water, forming 1 : 2-*ditolyl*iso*benzofuran*, m. p. 125°, crystallising in long, yellow needles. Ditoluoylbenzene, m. p. 184°, forms colourless crystals, and gives an intense magenta colour with sulphuric acid (compare Bauer, Abstr., 1905, i, 210). Its *monophenylhydrazone*, m. p. 171°, forms small, brilliant yellow prisms. Ditolylphthalazine, m. p. 221°, crystallises from alcohol in long, slender needles. o-*Ditolhydrylbenzene*, m. p. 118°, forms small, colourless spangles. 1 : 2-*Ditolyl*-1 : 2-*dihydro*iso*benzofuran*, m. p. 89°, separates from methyl alcohol in slender, colourless needles.

Ditolyl-o-*tolhydrylphenylcarbinol*,

$$C_6H_4Me\cdot CH(OH)\cdot C_6H_4\cdot C(C_6H_4Me)_2\cdot OH,$$

m. p. 138°, forms small, brilliant prisms, and in contact with sulphuric acid loses 2 mols. of water, giving 9 : 10-p-*ditolyl*-2-*methylanthracene*, which crystallises in yellow prisms and fluoresces violet in benzene and its homologues. On oxidation it gives 9 : 10-*dihydroxy*-9 : 10-*ditolyl*-2-*methyldihydroanthracene*, m. p. 207° (anhydrous), which crystallises with some alcohol in brilliant prisms, gives an indigo-blue coloration with sulphuric acid, and liberates iodine from potassium iodide.

Magnesium *a*-naphthyl bromide in ether reacts with phenyl-

phthalide, forming 2-*hydroxy*-1-*phenyl*-2-*naphthyl*-1 : 2-*dihydro*iso*benzofuran*. This was obtained as an oil, which, on oxidation, gave o-*benzoylnaphthoylbenzene*, m. p. 104°, in small, colourless crystals. o-*Toluoylnaphthoylbenzene*, m. p. 144°, crystallising in small, colourless prisms, was obtained similarly from the condensation product of magnesium α-naphthyl bromide and tolylphthalide. T. A. H.

Quinhydrones. WILHELM SIEGMUNDS (*J. pr. Chem.*, 1911, [ii], **83**, 553—555).—By the addition of a warm ethereal solution of the phenol to a warm solution of *p*-benzoquinone in petroleum, the following *quinhydrones* have been obtained: $3C_6H_4O_2,4C_6H_3(OH)_3$, m. p. 78°, black needles, from *p*-benzoquinone (2 mols.) and pyrogallol (1 mol.); $3C_6H_4O_2,4C_6H_3(OH)_3$, m. p. 164°, green needles, from *p*-benzoquinone (1 mol.) and hydroxyquinol (1 mol.);

$$3C_6H_4O_2,2C_6H_3(OH)_3,$$

m. p. 103°, red crystals, from *p*-benzoquinone (4 mols.) and phloroglucinol (1 mol.); $C_6H_4O_2,C_{10}H_6(OH)_2$, from *p*-benzoquinone (1 mol.) and 2 : 3-dihydroxynaphthalene (1 mol.), separates initially in pale red leaflets, finally in garnet-red needles, both forms having m. p. 78—80° (compare Abstr., 1909, i, 109). C. S.

Constitution of Quinhydrone-like Substances. ANGELO KNORR (*Ber.*, 1911, **44**, 1503—1506).—Richter's conception of quinhydrones as oxonium compounds (this vol., i, 136) is inapplicable to the quinhydrones obtained by Haakh from quinones and hydrocarbons (Abstr., 1910, i, 48). The author selects several of Richter's examples and shows that the constitutions ascribed to them are at variance with their properties. A true *imonium* compound,

$$NO_2\cdot C_6H_4\cdot O\cdot NH_2{:}C_6H_4{:}NH_2\cdot O\cdot C_6H_4\cdot NO_2,$$

m. p. 59° (decomp.), has been prepared from quinonedi-imine and *p*-nitrophenol in ether. It forms yellow crystals and lacks, therefore, the chief criterion of a quinhydrone, namely, an intense colour in comparison with those of its components. C. S.

Vat Dyes from α-Naphthaquinone. RUDOLF PUMMERER and KURT BRASS (*Ber.*, 1911, **44**, 1647—1656).—A number of substituted 2-amino-α-naphthaquinones have been prepared by the condensation of amino-compounds with α-naphthaquinone. On reduction with alkaline hyposulphite, the majority of these compounds yield vats which dye cotton without a mordant. The dyes are, however, of no technical importance, partly on account of their lack of vivid shades, and partly because of their insufficient fastness to chlorine and light.

From experiments on the behaviour of several leuco-compounds of vat-dyes towards vegetable fibres, the authors draw the conclusion that the production of fast colours is determined by the following two factors: (1) the affinity of the leuco-compounds for the fibre, and (2) the firmness with which the dye is mechanically fixed on the fibre when the leuco-compound is oxidised.

2-p-*Aminoanilino*-α-*naphthaquinone*, $\begin{matrix} C_6H_4\cdot CO \\ | \\ CO{-}CH \end{matrix}\!\!>\!C\cdot NH\cdot C_6H_4\cdot NH_2$,

obtained by reducing 2-*p*-nitroanilino-α-naphthaquinone with alkaline hyposulphite and oxidising the resulting solution with a current of air,

crystallises in dark violet prisms, m. p. 214° (not sharp); with strong sulphuric acid it gives a safranine-red solution, from which a yellowish-red *sulphate* is precipitated by water.

N-N′-*Di*-2-*α-naphthaquinonyl*-p-*phenylenediamine*,

$$C_6H_4(NH \cdot C_{10}H_5O_2)_2,$$

is prepared by heating *α*-naphthaquinone with *p*-phenylenediamine in glacial acetic acid solution; it forms a brownish-violet, crystalline powder, m. p. 250° (not sharp), and gives with alkaline hyposulphite a light yellow vat, in which cotton is dyed brownish-violet. It is oxidised with lead peroxide in xylene solution, yielding probably p-*benzoquinonedi*-2-*α-naphthaquinonyldi-imine*.

2-(4′)-*Diphenylylamino-α-naphthaquinone*, $C_{10}H_5O_2 \cdot NH \cdot C_6H_4Ph$, obtained by heating *α*-naphthaquinone and 4-aminodiphenyl in alcoholic solution, crystallises in red needles, m. p. 215°.

2-*Benzidino-α-naphthaquinone*, $C_{10}H_5O_2 \cdot NH \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2$, prepared from benzidine and *α*-naphthaquinone, crystallises in brown needles, m. p. 259°, and gives scarlet-red salts; the *acetyl* derivative forms violet crystals, m. p. 329° (decomp.).

2-o-*Tolidino-α-naphthaquinone* is a dark violet powder; the *acetyl* derivative, $C_{26}H_{22}O_3N_2$, crystallises in spindle-shaped prisms, m. p. 233°.

2-o : o′-*Dichlorobenzidino-α-naphthaquinone*, $C_{22}H_{14}O_2N_2Cl_2$, has m. p. 237° with previous sintering; the *acetyl* and *benzoyl* derivatives crystallise in plates having a coppery lustre, m. p. 264° and 302° respectively.

N-p-*Aminophenyl*-N′-p-2-*α-naphthaquinonylaminophenylcarbamide*, $C_{10}H_5O_2 \cdot NH \cdot C_6H_4 \cdot NH \cdot CO \cdot NH \cdot C_6H_4 \cdot NH_2$, prepared from *p*:*p*′-diaminodiphenylcarbamide and *α*-naphthaquinone in glacial acetic acid solution, has m. p. 348°.

4-*Amino*-4′-(2)-*α-naphthaquinonylaminobenzophenone*,

$$C_{10}H_5O_2 \cdot NH \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot NH_2,$$

prepared from 4 : 4′-diaminobenzophenone, crystallises in flat, brick-red prisms.

4-*Amino*-4′-(2)-*α-naphthaquinonylaminodiphenylmethane*,

$$C_{10}H_5O_2 \cdot NH \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot NH_2,$$

prepared from 4 : 4′-diaminodiphenylmethane, has m. p. 182°. F. B.

Preparation of 2:2′-Dianthraquinonylcarbamide. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 232739).—The preparation of arylanthraquinonylcarbamides has previously been described (this vol., i, 469); it is now found that the action of carbonyl chloride at 170° on a nitrobenzene solution of 2-aminoanthraquinone forms initially 2-anthraquinonylcarbamide chloride, which then combines with another molecule of the base, yielding 2 : 2′-*dianthraquinonylcarbamide*, which separates in small, orange crystals. F. M. G. M.

Condensation of Anthraquinone with Phenols. Wassili W. Scharwin [with K. A. Kusnezoff, W. A. Naumoff, A. L. Gandurin, N. I. Bjenkoff, and S. A. Dmitrieff] (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 562—574).—Most of this work has been already published (Abstr., 1903, i, 640; 1904, i, 1032), the new matter being as follows.

Tetrabromophenolanthrone (*tetrabromophenolanthraquinone*), $C_{26}H_{14}O_3Br_4$, forms colourless needles, m. p. 290°.

Dinitrophenolanthrone, $C_{26}H_{16}O_7N_2$, forms shining, yellow plates with a faint green tint, m. p. 236°; in alkaline solution it gives a pure, bright yellow coloration, which, as with other nitrophenols (compare Scharwin, Abstr., 1910, ii, 396), increases in intensity on dilution. *Tetranitrophenolanthrone*, $C_{26}H_{14}O_{11}N_4$, forms lemon-yellow needles, m. p. 278°, and, in an acid-bath, dyes wool and silk bright yellow. *Hexanitrophenolanthrone*, $C_{26}H_{12}O_{15}N_6$, was also prepared.

Dinitroresorcinolanthrone, $C_{26}H_{14}O_8N_2$, and *tetramethoxydiphenylanthrone*, $CO<\substack{C_6H_4\\C_6H_4}>C[C_6H_3(OMe)_2]_2$, were obtained as yellow powders; hydrolysis of the latter by means of aluminium chloride yields resorcinolanthrone. T. H. P.

Synthesis of Orthoquinones. CARL LIEBERMANN (*Ber.*, 1911, **44**, 1453—1455. Compare Liebermann and Zsuffa, this vol., i, 202, 387).—*p*-Ditolyl condenses with oxalyl chloride and aluminium chloride, yielding 2 : 7-dimethylphenanthraquinone together with 4 : 4′-dimethyldiphenic acid.

2 : 7-*Dimethylphenanthraquinone*, $C_{16}H_{12}O_2$, crystallises from alcohol in glistening, orange-red plates, m. p. 224°, and gives a green solution in concentrated sulphuric acid. The corresponding quinol is unstable, but yields a stable *diacetyl* derivative, $\begin{matrix}C_6H_3Me\cdot CH\cdot OAc\\ | \qquad\quad | \\ C_6H_3Me\cdot CH\cdot OAc\end{matrix}$, in the form of colourless, glistening plates, m. p. 202°.

4 : 4′-*Dimethyldiphenic acid*, $CO_2H\cdot C_6H_3Me\cdot C_6H_3Me\cdot CO_2H$, has m. p. 324°. The calcium salt crystallises in transparent prisms containing $2H_2O$. J. J. S.

Colloidal Chemical Observations on the Pyranthrone Vat Dyes. ROLAND SCHOLL (*Ber.*, 1911, **44**, 1448—1452).—Pyranthrone yields a purple-red vat dye when reduced with a hot alkaline solution of sodium hyposulphite (Abstr., 1910, i, 271) and a yellow cherry-red vat when reduced at the ordinary temperature. Both products react with *p*-bromobenzoyl chloride, yielding di-*p*-bromobenzoyltetrahydropyranthrones, which differ somewhat in appearance, but when the compound from the cherry-red vat is crystallised several times from nitrobenzene, it has the same appearance as the product from the purple-red vat. The conclusion drawn is that the cold vat consists essentially of the same tetrahydropyranthrone as the hot vat, and that its cherry-red colour is due to a small amount of impurity, namely, colloidal pyranthrone, which forms a colloidal complex with the vat.

Experiments are described which support this view.

The formation of lighter tones by immersing fabrics dyed with pyranthrone in boiling soap solution is shown to be due to a process of oxidation, and the same results can be obtained by exposing the dyed fabric to a 10% solution of sodium hydroxide containing a little potassium ferricyanide and to dilute alkali and atmospheric oxygen. The deeper tone can be restored by treatment with alkaline hypo-

sulphite solution, slowly at the ordinary temperature and more rapidly by warming.

Tetrahydropyranthrone can be obtained by allowing the vat, obtained by using hot alkaline hyposulphite, to cool in an atmosphere of hydrogen and then precipitating with dilute acetic acid. When dry, the precipitate has a yellowish-red colour, and gives a violet-red solution in sodium hydroxide.

When kept for some hours, the precipitate becomes darker, and yields an opalescent, brown solution with sodium hydroxide, probably containing dihydropyranthrone, as it turns yellow when shaken with air, owing to the formation of pyranthrone, and violet-red when treated with hyposulphite solution. J. J. S.

β-Camphor (Bornylone) from Bornylenecarboxylic Acid. JULIUS BREDT and W. HILBING (*Chem. Zeit.*, 1911, **35**, 765).—An account of the synthesis of β-camphor,

$$\begin{array}{lcl} CH_2\text{—} & CH & \text{——}CO \\ | & | & \quad | \\ | & CMe_2 & \quad | \\ | & | & \quad | \\ CH_2\text{—} & CMe & \text{——}CH_2 \end{array}$$

, from bornylenecarboxylic acid (Bredt, Abstr., 1906, i, 680; 1909, i, 499). *Bornylenecarboxyl chloride*, $C_{10}H_{15}\cdot COCl$, b. p. 114—115°/14 mm., when treated with hydrazine hydrate, yields the corresponding *hydrazide*, $C_{10}H_{15}\cdot CO\cdot NH\cdot NH_2$, m. p. 109—110°, which is converted, according to the method of Curtius, into the *azide*, $C_{10}H_{15}\cdot CO\cdot N_3$, and then into *β-iminocamphor*. On hydrolysis with acids, this yields β-camphor, b. p. 213·1—213·4°, m. p. 184—185°, which is identical with the epicamphor (of m. p. 165°) recently described by Lankshear and Perkin (Proc., 1911, **27**, 166).

On oxidation with nitric acid, β-camphor yields camphoric acid.

The oxime has m. p. 103—104°; the semicarbazone, m. p. 237° (compare Lankshear and Perkin, *loc. cit.*).

Wagner's (*Chem. Zeit.*, 1903, **27**, 721) β-camphor consists mainly of ordinary camphor. F. B.

Hydrogenation of Limonene. GUSTAVE VAVON (*Compt. rend.*, 1911, **152**, 1675—1677).—Determination of the rate at which limonene absorbs hydrogen in presence of platinum-black shows that the hydrogenation takes place in two stages, enabling the dihydride or tetrahydride to be obtained at will. *Dihydrolimonene*, $C_{10}H_{18}$, has physical constants approaching those of Δ^1-tetrahydro-*p*-cymene (carvomenthene): b. p. 175—177°, n_D^{18} 1·4563, D_4^{18} 0·8246, $[\alpha]_{\lambda 578}$ +118°, $[\alpha]_{\lambda 436}$ +234°; the *dibromide*, $C_{10}H_{18}Br_2$, has b. p. 136—140°/16 mm., n_D^{21} 1·5236, D_4^{21} 1·459, $[\alpha]_{\lambda 578}$ +49°, $[\alpha]_{\lambda 436}$ +100°. The *nitrosochloride*, $C_{10}H_{18}ONCl$, remarkable for its high rotatory power, has m. p. 95—96°, $[\alpha]_{\lambda 578}$ +344°, $[\alpha]_{\lambda 436}$ +724°; the racemic form has been described by Wallach (this vol., i., 470). W. O. W.

Chemistry of Caoutchouc. Theory of Vulcanisation. D. SPENCE and J. H. SCOTT (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 304—312).—The properties of vulcanised caoutchouc have been examined in relation to the chemical and the absorption theories of

vulcanisation. It is found that a portion of the sulphur cannot be removed either by the action of acetone or hot sodium hydroxide solution. When the vulcanised caoutchouc is treated with bromine by Budde's method, the product obtained contains sulphur and bromine in proportions which indicate that four atoms of bromine in the tetrabromide, $C_{10}H_{16}Br_4$, are in fact replaced by two atoms of sulphur. This equivalence of the "fixed" sulphur and the bromine is regarded as strong evidence in favour of the chemical combination of the "fixed" sulphur. Experiments, in which the quantities of sulphur removed by acetone in successive equal extraction periods were measured, indicate that a portion of the so-called "free" sulphur is adsorbed. The curves obtained by plotting the successive quantities of extracted sulphur against the period of extraction are in agreement with the requirements of an exponential adsorption equation.

From these results the following conclusions are drawn: (1) the "fixed" sulphur is chemically combined with the caoutchouc; (2) the "free" sulphur, that is to say, the portion which can be removed by solvents, is, in part, adsorbed, the remainder being present in the non-adsorbed condition. The amount of the non-adsorbed free sulphur is dependent on the conditions of the vulcanising process.

H. M. D.

Essential Oil of Bupleurum fructicosum. LUIGI FRANCESCONI and G. SANNA (*Gazzetta*, 1911, 41, i, 395—414).—The authors have examined the yield and properties of the essential oil obtained from specimens of *Bupleurum fructicosum* in different stages of development and from different localities.

The value of D^{15} varies from 0·8257 to 0·8692; the diminution per 1° rise of temperature is about 0·0008. The specific rotation varies for plants from different places and for the essences yielded by different organs; its maximum and minimum were found to be +45·5° and +19·72° respectively. The rotation diminishes with lapse of time, whilst the density increases. The value of n_D is 1·4783—1·4862, and the b. p. varies for any sample between about 167° and 200°.

In the air and light, it readily oxidises, forming a resinous substance, and this change may also be induced by heating in absence of air for three to four hours at 210°.

The yield of essential oil increases with the development of the plant, and during the periods of advanced and complete inflorescence is greater for the flowers than for the leaves. The density, rotation, and index of refraction increase up to the beginning of flowering and then diminish. The ester content is greater in plants growing at great altitudes, and diminishes with increase of the moisture in the air of the region. The rotatory power varies inversely, and the density directly, with the ester content. The amount of free alcohol is greater in the flowers than in the leaves, and increases in relation to the combined alcohol as flowering progresses. The principal constituents of the essential oil are hydrocarbons. T. H. P.

Essential Oil of Wallflowers. KUMMERT (*Chem. Zeit.*, 1911, 73, 667—668).—With low-boiling solvents, the blooms of *Cheiranthus Cheiri* yield a dark unctuous extract, which, when freed from fatty

matter by strong alcohol and distilled with steam, gives about 0·06% of a yellow, evil-smelling oil, showing in alcoholic solution a slightly blue fluorescence. Distilled under low pressure (3 mm.), less than 1% comes over at 40°, consisting mainly of tear-producing sulphur and nitrogen compounds, resembling mustard oil, which probably unite in the seed-pods to complex molecules, producing the substance cheirolin discovered by Schneider (Abstr., 1909, i, 826; 1910, i, 658). The higher fractions contain aldehydes and ketones, which were separated by their carbazones. These, on treatment with oxalic acid, gave a distinct odour of violets (irone?) and hawthorn (anisaldehyde?). The oil, freed from aldehydes and ketones, was saponified with alcoholic potash, washed, steam-distilled, dried in vacuum, and heated in the water-bath with benzene and phthalic anhydride. The primary alcohols nerol, geraniol, and benzyl alcohol were identified. In the neutral oil, linalool was detected. From the potassium hydroxide extract were obtained phenols (*p*-cresol?) and lactones (coumarin-like substances), acetic, salicylic and anthranilic acids.

The last small fractions contained methyl anthranilate and indole, along with substances smelling like pyridine. J. D. K.

Meliatin, a New Glucoside Hydrolysable by Emulsin, obtained from the Marsh Trefoil. Marc Bridel (*Compt. rend.*, 1911, **152**, 1694—1696).—A new glucoside, *meliatin*, $C_{15}H_{22}O_9$, has been extracted from the marsh trefoil (*Menyanthes trifoliata*) by extraction with alcohol. The compound occurs in colourless crystals with a bitter taste, m. p. 222° (corr.), $[\alpha]_D$ $-81·96°$ in aqueous solution. It undergoes hydrolysis by emulsin with production of dextrose. W. O. W.

Preparation of Mixed Formic Acetic Esters of Aloins. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 233326).—When aloin is heated at 100° with a mixture of formic and acetic acids (or with formic acetic anhydride) in the presence of zinc chloride, mixed esters are produced.

The *ester*, containing two formyl and three acetyl residues, forms an almost tasteless, yellow powder, decomposing at 75—90°.

F. M. G. M.

Chlorophyll. XVI. The Primary Decompositions of Chlorophyll. Richard Willstätter and Max Utzinger (*Annalen*, 1911, **382**, 129—194).—Crystalline chlorophyll (ethylchlorophyllide) (Willstätter and Benz, Abstr., 1908, i, 199; Willstätter and Stoll, this vol., i, 142) consists of two definite compounds, *a* and *b* (compare Willstätter and Isler, this vol., i, 392). The analysis of the product dried over phosphoric oxide in the vacuum of a water-pump agrees with the formula $C_{38}H_{44}O_7N_4Mg$, not $C_{38}H_{42}O_7N_4Mg$; when heated at 100—105°/0·001—0·01 mm., a further loss of about 5% occurs, probably due to water and ether, and the residue has a composition corresponding with the formula $C_{37}H_{39}O_{5·5}N_4Mg$. It is suggested that this probably consists of a mixture of the chlorophyllide-*a*, $C_{37}H_{39}O_{5·5}N_4Mg$, and chlorophyllide-*b*, $C_{37}H_{37}O_{6·5}N_4Mg$ (or $C_{37}H_{39}O_{6·5}N_4Mg$), in the ratio 2·5 : 1. The *a* compound is regarded as a mixture of practically

equal parts of the lactam, $C_{37}H_{38}O_5N_4Mg$, and the lactam hydrate, $C_{37}H_{40}O_6N_4Mg$.

The ethylchlorophyllide, dried at 100—105°, yields methyl and ethyl iodides in molecular proportions when heated with hydriodic acid. It is shown that these two alkyl iodides can be recognised and separated by conversion into quaternary ammonium salts. This can be accomplished by the aid of dimethylaniline in the absence of alcohol, or by means of an alcoholic solution of trimethylamine. Dimethylaniline reacts with methyl iodide much more readily than with ethyl iodide; for example, after six hours 95% of the methyl iodide has combined, whereas only 8% of the ethyl iodide has reacted. The separation can also be accomplished by means of the different solubilities of the two quaternary ammonium iodides. Phenyltrimethylammonium iodide is very sparingly soluble in chloroform, whereas phenyldimethylethylammonium iodide, m. p. 136°, dissolves with the greatest readiness. With trimethylamine the separation is even more marked, especially with absolute alcohol as solvent. One gram of tetramethylammonium iodide dissolves in 1060 grams of absolute alcohol, whereas 1 gram of trimethylethylammonium iodide dissolves in 1·23 grams of absolute alcohol.

A slightly modified method for the isolation of ethylchlorophyllide is described; it consists in removing the colouring matter from its alcoholic solution by ether, drying with sodium sulphate, evaporating until the solution has a thick consistency, then mixing well with talc, keeping for a day, then filtering, and washing well with ether. The mixture of talc and coloured crystals, which is free from yellow pigments, is then extracted with alcohol (not absolute), mixed rapidly with ether, and the alcohol removed by washing. The ethereal solution when evaporated slowly yields crystals of ethylchlorophyllide. Two points of importance in the isolation are: (*a*) sufficient time must be allowed for the complete ethanolysis of the original chlorophyll to ethylchlorophyllide (Willstätter and Stoll, this vol., i, 141); (*b*) the alcohol must contain water; previously 96% alcohol was recommended, but 10% of water increases the rate of alcoholysis.

Different specimens of ethylchlorophyllide differ somewhat in appearance; in solution under the microscope some are bluish-green and others yellowish-green. These differences are probably due to the different amounts of the *a* and *b* compounds present. Some preparations are sparingly soluble in ether (1 gram in 2·5 litres), but the products dried at 100° under reduced pressure are extremely readily soluble in absolute ether, although when hydrolysed by alkali they give the characteristic brown phase.

Ethylchlorophyllide undergoes a change when kept for some time in absolute ethyl or methyl alcohol, and the products formed no longer give the brown phase when hydrolysed by alkalis. The altered compound dissolves readily in ether, cannot be crystallised, but is thrown down as a bluish-black powder on the addition of light petroleum to its ethereal solution. When fractionally precipitated, the first fraction is more yellowish-green and the last distinctly blue. Analyses of the product formed by the action of methyl

alcohol agree with the view that half a molecule of water and half a molecule of methyl alcohol have combined with the ethylchlorophyllide.

Ethylphæophorbide, the product free from magnesium formed by the action of cold acids on ethylchlorophyllide, consists of two distinct compounds. It is obtained crystalline by the action of a saturated ethereal solution of hydrated oxalic acid on an ethereal solution of the chlorophyllide. At the end of two days, large brownish-black plates with a metallic lustre are deposited (Fraction I), and from the mother liquors, after removal of oxalic acid, long, pointed prisms are obtained (Fraction II). Both fractions can be recrystallised by solution in chloroform, mixing with a little ether, and pouring into much ether; fraction II can also be crystallised from ether. Fraction I is extremely sparingly soluble in cold alcohol or ether; its solutions in most organic solvents have a reddish-olive colour, but its solution in formic acid is bluish-green. When hydrolysed with alcoholic potash, it yields much phytorhodin-*g*, together with phytochlorin-*e*. Fraction II is more readily soluble in ether; its solutions are generally olive-green, but that in formic acid is blue. When hydrolysed with alkalis, it yields mainly phytochlorin-*e*, together with a very small amount of phytorhodin. Molecular-weight determinations of ethylchlorophyllide, ethylphæophorbide, and other products by cryoscopic and ebullioscopic methods indicate that they have not the double formulæ.

When chlorophyll-*a* in light petroleum solution is hydrolysed with 7% methyl-alcoholic potassium hydroxide, the potassium salt of chlorophyllin, $C_{34}H_{31}O_6N_4MgK_3$ (compare Willstätter and Fritzsche, Abstr., 1910, i, 126), separates as glistening, dark blue plates, which appear pure green under the microscope in transmitted light. The salt is not quite pure, and contains about 1% of methoxyl.

When decomposed with hydrochloric acid, it yields phytochlorin-*g*, which can be extracted from its ethereal solution by 11% hydrochloric acid.

When the chlorophyllin salt is heated in sealed vessels with alcoholic potassium hydroxide, it yields glaucophyllin, then rhodophyllin, and finally pyrrophyllin (Willstätter and Fritzsche, *loc. cit.*). A different chlorophyllin, iso*chlorophyllin*, is formed when chlorophyll-*a* in pyridine solution is hydrolysed with warm alcoholic potassium hydroxide. The potassium salt could not be isolated in the form of good crystals, and contained too little nitrogen and magnesium. The *calcium* salt forms a pale green, flocculent precipitate. When decomposed with hydrochloric acid, the *iso*chlorophyllin yields phytochlorin-*e*, and when heated with alcoholic potassium hydroxide at 150°, it yields a phyllin the alkaline and ethereal solutions of which are deep blue. With alcoholic potassium hydroxide at 225—230°, it yields a phyllin identical with or closely allied to phyllophyllin. The ammonium and calcium salts are soluble in ether, and the calcium salt sparingly soluble in chloroform.

Phytochlorin-*e* can be obtained by hydrolysing crude chlorophyll extract with barium hydroxide, dissolving the barium salt of *iso*-chlorophyllin in ether, and shaking with 16% hydrochloric acid.

Alcoholic potassium hydroxide can react with phæophytin and ethylphæophorbide in two different ways, according to the conditions of the experiment.

With concentrated alcoholic potassium hydroxide, either cold or hot, the products are phytochlorin-*e* and phytorhodin-*g*. By the action of alcoholic potash on an ethereal solution of alkylphæophorbides, phytochlorin-*g* is formed together with a faintly basic phytorhodin—phytorhodin-*i* or a similar compound. These two processes correspond with the hydrolysis of chlorophyll by hot and by cold potassium hydroxide solution.

The analyses of various specimens of phytochlorin-*e* do not agree, and this is shown to be due to the fact that the compounds exist in two forms, which differ in the amount of water they contain, namely, $C_{34}H_{34}O_5N_4$ and $C_{34}H_{36}O_6N_4$, termed respectively the *lactam* and *lactam-hydrate*. It is possible that the two can unite to form a definite compound, which would be a half hydrate like many other chlorophyll derivatives.

In the isolation of the hydrate, it is essential that the method of extraction and purification should not entail prolonged treatment with hydrochloric acid, as this converts the hydrate into the lactam. The hydrate forms compact, opaque, crystalline plates with a violet lustre; the lactam, small, glistening plates which appear black to the eye. They are doubly refractive, and the colours in transmitted light are pale green, olive-green, and brown. Both compounds lose in weight when heated at 105°/0·01 mm. The lactam loses some 3%, and the hydrate 0·5 to 1%. The hydrate is quite stable, and is unaltered at the end of nine months. The lactam crystals are also stable, but after drying in a desiccator they undergo decomposition when kept; at the end of nine months an appreciable amount of a rhodin, probably phytorhodin-*h*, is present, together with phytochlorin-*f*. The lactam dissolves more readily than the hydrate in most solvents. The hydrate is extremely sparingly soluble in cold alcohol, and is insoluble in chloroform. Its solution in formic acid is blue and in pyridine olive-coloured. Concentrated hydrochloric acid does not decompose phytochlorin-*e*, but concentrated sulphuric acid transforms it into an amorphous product insoluble in ether. With acetic anhydride, the phytochlorin yields glistening, bluish-black, rhombic plates, and when oxidised with chromium trioxide in sulphuric acid solution, it yields a mixture of acid and neutral products, including methylethylmaleinimide and the imide of hæmatic acid. When heated with crystallised phosphoric acid at 140°, it yields phylloporphyrin, but at 100° it yields only a small amount of phylloporphyrin, together with phytochlorin-*h*, which dissolves in dilute hydrochloric acid, giving a reddish-violet solution. It is formed from the original phytochlorin by the elimination of carbon dioxide. The following salts of phytochlorin-*e* have been prepared: $C_{34}H_{33}O_6N_4K_3$, brown, rectangular plates; $C_{34}H_{33 \cdot 5}O_6N_4Cs_{2 \cdot 5}$ and $C_{34}H_{35}O_6N_4 \cdot NH_4$. The *trimethyl* ester, $C_{31}H_{33}N_4(CO_2Me)_3$, obtained from the potassium salt and methyl sulphate, separated in steel-blue, felted prisms, m. p. 188—190°. The compound is also partly esterified by methyl alcohol and hydrogen chloride.

Phytochlorin-*f* (Willstätter and Isler, this vol., i, 392; Willstätter and Hocheder, Abstr., 1907, i, 785) has not been obtained from chlorophyllin-*a*. It has the formula $C_{34}H_{34}O_5N_4$, and loses but little in weight when dried at 105° under reduced pressure, and is sparingly soluble in most solvents, with the exception of formic acid and pyridine. The solution of the ammonium salt in ether has a brilliant green colour, and the solution in hydrochloric acid (10%) has a pure blue colour. The *caesium* salt, $C_{34}H_{31\cdot5}O_5N_4Cs_{2\cdot5}$, forms glistening, steel-blue prisms; the *methyl* ester, $C_{36}H_{36}O_4N_4$(?), forms blue, monoclinic, six-sided plates or prisms, and is less basic than the acid.

Phytochlorin-*g* is formed also when chlorophyll-*a* is kept for some time in light petroleum, and then hydrolysed with alcoholic potassium hydroxide and acidified. Its ethereal solution is olive-green, but turns brown when kept. The hydrochloric acid number is 10—11, and the solution in acid is bluish-green. When evaporated and warmed for a short time with alcohol, an unstable, brilliant red product is formed. When heated with alcoholic potassium hydroxide in silver vessels at 140—150°, phytochlorin-*g* yields a dicarboxylic product similar to glaucoporphyrin (Willstätter and Fritzsche, Abstr., 1910, i, 127); its hydrochloride is, however, less soluble, and the colours of its solutions are somewhat different. With alcoholic potassium hydroxide at 225—230°, phytochlorin-*g* yields pyrroporphyrin. Phytochlorin-*f*, when heated for seven hours at 140—150° with alcoholic potassium hydroxide, yields rhodoporphyrin, and at 200° yields pyrroporphyrin. Phytochlorin-*e* and alcoholic potassium hydroxide at 140—150° yield the monocarboxylic phylloporphyrin, the *methyl* ester of which, $C_{33}H_{38}O_2N_4$, crystallises from ether or acetone, has m. p. 224° after sintering at 220°, and acid number 1—1·25.

Phytorhodin-*g*, $C_{34}H_{34}O_7N_4$, is formed from the *b*-chlorophyll component of all plants by hydrolysing the phæophytin or phæophorbide in undiluted form with alkali. It is also formed from *iso*chlorophyllin and acid, and crystallises in compact, glistening, black, six-sided prisms, and appears to be a tribasic acid. A hydrated form also exists, $C_{34}H_{36}O_8N_4$. It is a strongly acid compound, and is removed from its ethereal solution by 0·001% ammonia. Its solution in dilute alcoholic potassium hydroxide has a deep red colour, but in concentrated, a green colour. The *potassium* salt,

$$C_{34}H_{31}O_7N_4K_3,$$

blackish-brown plates, *caesium* salt, $C_{34}H_{31}O_7N_4Cs_3$, rhombic plates, and *methyl* ester, $C_{37}H_{40}O_7N_4$, glistening, black, rectangular plates and prisms, m. p. 207—210°, have been prepared.

Phytorhodin-*i*, $C_{34}H_{32}O_6N_4$, the feebly basic phytorhodin previously described (this vol., i, 392), crystallises in brown or black, microscopic plates; its ethereal solution is brownish-red, and its solution in hydrochloric acid green. Its *potassium* salt is sparingly soluble in water. With alcoholic potassium hydroxide at 150°, it yields a dibasic porphyrin similar to rhodoporphyrin, and at 200° the monobasic pyrroporphyrin.

The relationships of many of the compounds are discussed.

J. J. S.

Dibasic Ketonic Acids. III. EDMOND E. BLAISE and HENRI GAULT (*Bull. Soc. chim.*, 1911, [iv], 9, 588—592).—This paper gives in greater detail, with some modifications, the results described already (Abstr., 1908, i, 713; 1909, i, 134).

Ethyl dioxalylsuccinate on hydrolysis by hydrochloric acid in the cold furnishes 3-hydroxy-2-pyrone-6-carboxylic acid, m. p. 87° (approx.), which crystallises in colourless needles, gives a violet coloration with ferric chloride, a green coloration with pine wood moistened with hydrochloric acid, and reduces ammoniacal silver nitrate slowly in the cold and immediately on warming. When heated at 150°, it furnishes *iso*pyromucic acid (3-hydroxy-2-pyrone), m. p. 87°, by loss of carbon dioxide (*loc. cit.*, Chavanne, Abstr., 1904, i, 82). In view of these results the authors suggest that the lactone and its derivatives obtained by Wislicenus and Boeckler (Abstr., 1895, i, 506) by the action of alkalis on ethyl dioxalylsuccinate should be represented by the following formulæ:

$$CO_2Et\cdot C(OH){:}C(CO_2Et)\cdot CH(CO_2Et)\cdot CO\cdot CO_2Et \longrightarrow$$

$$\begin{array}{l} CO_2Et\cdot C{:}C(CO_2Et) \\ CO_2Et\cdot CH\cdot CO{-}CO \end{array} \!\!>\! O \longrightarrow$$

$$CO_2H\cdot C(OH){:}C(CO_2Et)\cdot CH(CO_2Et)\cdot CO\cdot CO_2H.$$

T. A. H.

Migration of Phenyl in the Synthesis of Phenylated Coumarones. Phosphorus Tribromide as a Reducing Agent. III. RICHARD STOERMER (*Ber.*, 1911, 44, 1853—1865. Compare Abstr., 1904, i, 181; 1907, i, 446).—Aromatic γ-lactones, such as the lactone of phenyl-*p*-hydroxytolylacetic acid, when heated with phosphorus tribromide under ordinary pressure at a high temperature form 2-phenylated coumarones, whereas above 200° under pressure 1-phenylated compounds are also formed. It is supposed that an intermediate unsaturated compound is formed and not a brominated phenylcoumarone, which, when prepared in another manner, is not altered on heating with phosphorus tribromide. Similarly, 2-phenylcoumarone is unaltered by heating with phosphorus tribromide.

The lactone of dibromohydroxydiphenylacetic acid could not be converted into bromophenylcoumarone in this manner.

The tendency of the phenyl group to wander to position (1) is but small, and it is destroyed by the introduction of substituents.

The synthesis of 1-phenylcoumarone has been effected from homosalicylaldehyde and chlorophenylacetic acid in order to establish its constitution. Characteristic of this is the yellow coloration with concentrated sulphuric acid, which soon turns green.

1-Bromo-2-phenylcoumarone interacts very readily with nitrous fumes, forming 1-nitro-2-phenylcoumarone. This is still more conveniently prepared by dissolving the brominated coumarone in acetic acid, adding a little nitric acid and sodium nitrite, and warming until the bromine vapour has all been given off. On pouring into water, the nitro-compound is now obtained pure. Presumably an additive product with nitrogen trioxide is first formed, from which nitrosyl bromide is subsequently eliminated.

With phosphoryl chloride under pressure, 1-chloro-2-phenyl-

coumarone is obtained, and no migration of phenyl takes place. This product cannot be reduced to the chlorine-free compound.

[With CLAUS DECKER.]—2-*Phenyl*-4-*methylcoumarone*,

$$C_6H_3Me{<}\substack{O\\CPh}{>}CH,$$

has b. p. 193°/20 mm., does not solidify on cooling, and gives an intense red coloration with concentrated sulphuric acid. It forms 2-phenyl-4-methylcoumarone on reduction.

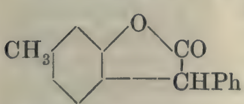
1-*Phenyl*-4-*methylcoumarone*, $CH_3\cdot C_6H_3{<}\substack{O\\CH}{>}CPh$, forms colourless, matted needles, m. p. 129°.

1-*Bromo*-2-*phenyl*-4-*methylcoumarone* crystallises in stellar aggregates of needles, m. p. 65°, which show a faint red coloration with concentrated sulphuric acid.

1-*Nitro*-2-*phenyl*-4-*methylcoumarone* forms radially-grouped, yellow needles, m. p. 115—116°.

1-*Bromo*-2-*phenylcoumarone* is an oil of sweet odour, b. p. 195°/20 mm. 1-*Nitro*-2-*phenylcoumarone* separates in long, yellow needles, m. p. 105°. The *bromo*-derivative of 1-phenylcoumarone has b. p. 203°/23 mm., crystallising in lustrous, silvery platelets, m. p. 81°. Nitrous acid is without action on it.

The lactone of phenyl-*m*-hydroxytolylacetic acid (annexed formula) when heated with phosphoryl chloride at 130° forms 1-*chloro*-2-*phenyl*-5-*methylcoumarone*, b. p. 175°/10 mm., crystallising in needles of silvery lustre, m. p. 85·5°. On reduction of this chloride, or of the corresponding bromide, 2-*phenyl*-5-*methylcoumarone* is obtained in small, colourless needles, m. p. 45°, b. p. 170°/14 mm. This, when brominated in acetic acid, is converted into 4(?)-*bromo*-5-*methyl*-2-*phenylcoumarone*, which crystallises in short, pointed needles, m. p. 125°.



Phenylmethylcoumarone when heated with alkali hydroxide at 200° under pressure yields *phenyl*-m-*hydroxytolylethylene*,

$$OH\cdot C_6H_3Me\cdot CPh{:}CH_2,$$

a colourless oil, b. p. 205°/20 mm., soluble in alkali, and becoming intense red with concentrated sulphuric acid.

2-*Phenyl*-5-*methylcoumarone*, obtained by the action of phosphorus tribromide on the lactone of phenyl-*m*-hydroxytolylacetic acid, forms short needles, m. p. 31°, b. p. 168°/18 mm., and gives an intense orange coloration with concentrated sulphuric acid.

The isomeric 1-*phenyl*-5-*methylcoumarone*, obtained on more strongly heating, crystallises in silvery needles, m. p. 135·5°, and gives a yellow coloration with sulphuric acid, changing to dark green. This compound is identical with that obtained on condensing phenylchloroacetic acid with *m*-homosalicylaldehyde. Accordingly, the formula of the lactone of phenyl-*m*-hydroxytolylacetic acid is established as that given above.

1-*Bromo*-2-*phenyl*-5-*methylcoumarone* has m. p. 95°; the corresponding 1-*nitro*-derivative forms small, yellow crystals, m. p. 119—120°.

The *lactone* of o-*hydroxyphenylanisylacetic acid*, prepared from anisaldehyde cyanohydrin, phenol, and sulphuric acid, forms colourless

needles, m. p. 178°. The corresponding anisylcoumarone could not be obtained.

p-*Hydroxytolylanisylacetic acid lactone* forms colourless plates, m. p. 135°. On heating with phosphorus tribromide, 2-*anisyl*-4-*methylcoumarone* is obtained in matted needles, m. p. 73·5°; this shows a strong eosin coloration with strong sulphuric acid.

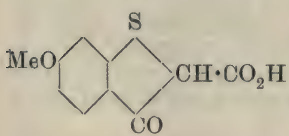
[With KARL HILDEBRANDT.]—The *lactone* of p-*chloro*-o-*hydroxydiphenylacetic acid* forms colourless needles, m. p. 125°; the corresponding *bromo*-compound is very similar, m. p. 123°. On heating with phosphoryl chloride, 1-*chloro*-2-p-*chlorophenylcoumarone* is obtained in long, silvery needles, m. p. 122°.

2-p-*Chlorophenylcoumarone*, m. p. 34°, gives an orange coloration with sulphuric acid; the isomeric 1-phenyl derivative could not be obtained.

1-*Chloro*-2-p-*bromophenylcoumarone* forms long, lustrous needles, m. p. 119°.

2-p-*Bromophenylcoumarone* crystallises in long, matted needles, m. p. 38°, giving an orange-red coloration with sulphuric acid. The 1-phenyl compound could not be detected. E. F. A.

Preparation of Alkyloxy- and Alkylthio-derivatives of 3-Hydroxy-(1)-thionaphthen-2-carboxylic Acid. KALLE & Co. (D.R.-P. 232377. Compare Abstr., 1908, i, 451, 797).—The preparation of 3-hydroxy-(1)-thionaphthen-2-carboxylic acid from phenyl-o-carboxymethylthiolbenzoic acid has been recorded previously, and the preparation of its alkyloxy- and alkylthio-derivatives containing the substituted group in the benzene ring is now described.



3-*Keto*-6-*methoxy*-(1)-*thionaphthen*-2-*carboxylic acid* (annexed formula), yielding a yellow *nitroso*-derivative and converted by boiling dilute hydrochloric acid into 3-*keto*-6-*methoxy*-(1)-*thionaphthen* (needles, m. p. 118—119°), was prepared by the following series of operations.

o-Amino-*p*-cresol was acetylated, and subsequently methylated with methyl sulphate in alkaline solution, yielding o-*acetylamino*-p-*tolyl methyl ether*, needles, m. p. 96°; this was oxidised to 2-*acetylamino*-4-*methoxybenzoic acid*, colourless needles, m. p. 197—199°, which by successive hydrolysis, diazotisation, xanthogenation, and treatment with chloroacetic acid, yielded 6-*methoxyphenylthioglycol*-o-*carboxylic acid*, needles, m. p. 224—225°; this acid when fused at 180—200° with sodium hydroxide yielded the foregoing 6-methoxy-3-oxy-(1)-thionaphthen-2-carboxylic acid.

4-*Acetylaminophenol*-3-*carboxylic acid*, m. p. 224—226°, by similar treatment yielded 2-*carboxymethylthiol*-5-*methoxybenzoic acid*, yellow prisms, m. p. 197—199°, which was subsequently converted by fusion with alkali into 3-*keto*-5-*methoxy*-(1)-*thionaphthen*-2-*carboxylic acid*; this acid forms a *nitroso*-derivative (yellow needles, m. p. 208—209°), and is converted by boiling dilute hydrochloric acid into 3-*keto*-5-*methoxy*-(1)-*thionaphthen*, yellow needles, m. p. 102—104°.

3-*Keto*-6-*ethylthiol*-(1)-*thionaphthen*, yellow needles, m. p. 84—85°,

yielded a *nitroso*-derivative, and the following intermediate compounds were obtained in its preparation. 4-*Acetylaminoanthranilic acid*, m. p. 193—194°. 2-*Carboxymethylthiol*-4-*acetylaminobenzoic acid*, colourless needles, m. p. 249° (decomp.), which on hydrolysis, diazotisation, and xanthogenation yielded 2-*carboxymethylthiol*-4-*ethylxanthatobenzoic acid*,

$$EtO\cdot CS_2\cdot C_6H_3(S\cdot CH_2\cdot CO_2H)\cdot CO_2H,$$

a yellowish-red powder, which was converted into 2-*carboxymethylthiol*-4-*ethylthiolbenzoic acid*, yellow needles, m. p. 188°. 3-*Keto*-6-*ethylthiol*-(1)-*thionaphthen*-2-*carboxylic acid*, $SEt\cdot C_6H_3{<}{}^{S}_{CO}{>}CH\cdot CO_2H$, a colourless powder, yielded a *nitroso*-derivative, glistening, reddish-yellow needles, m. p. 176°.

3-*Keto*-5-*methylthiol*-(1)-*thionaphthen*, yellow needles, m. p. 81—82°, yielded a *nitroso*-derivative, m. p. 178°, and was prepared through the following compounds: 2-*carboxymethylthiol*-5-*acetylaminobenzoic acid* (obtained from 5-acetylaminoanthranilic acid), colourless needles, m. p. 249—250°; 2-*carboxymethylthiol*-5-*ethylxanthatobenzoic acid*, yellow crystals; 2-*carboxymethylthiol*-5-*methylthiolbenzoic acid*, yellow needles, m. p. 195°; and 3-*keto*-5-*methylthiol*-(1)-*thionaphthen*-2-*carboxylic acid*, which has no characteristic melting point. F. M. G. M

[Preparation of Thionaphthen Derivatives.] KALLE & Co. (D.R.-P. 232995).—*Bistolylthioglycollic acid*, glistening leaflets, m. p. 167—168°, prepared by methods previously described (Abstr., 1880, 476), is converted by treatment with chlorosulphonic acid into *bisketotolylthionaphthen*, and *bisketophenylthionaphthen* is obtained in a similar manner from bisphenylthioglycollic acid. These oxythionaphthen derivatives furnish blue dyes on oxidation, and condense with compounds containing the groups CO–, CS–, C:NR, C:N·NHR, and CX_2– (where R is alkyl and X a halogen). F. M. G. M.

Salts of Arginine. FRITZ WEISS (*Zeitsch. physiol. Chem.*, 1911, 72, 490—493).—dl-*Arginine aurichloride*,

$$C_6H_{14}O_2N_4,2HCl,AuCl_3,\tfrac{1}{2}H_2O,$$

separates from water in brownish-red, nodular masses, m. p. 105—115°. d-*Arginine aurichloride*, $C_6H_{14}O_2N_4,2HAuCl_4,1\tfrac{1}{2}H_2O$, is somewhat more soluble in water than the *dl*-salt; it sinters at 140°, and has m. p. 160°. The *acid sulphate*, $C_6H_{14}O_2N_4,H_2SO_4,H_2O$, forms hard, crystalline crusts from dilute alcohol with no definite m. p. The corresponding *d*-salt forms a deliquescent, crystalline powder.

J. J. S.

Nitroclupeine. ALBRECHT KOSSEL and E. L. KENNAWAY (*Zeitsch. physiol. Chem.*, 1911, 72, 486—489).—By the addition of well cooled fuming nitric acid (1 c.c.) to a well stirred mixture of clupeine sulphate (2 grams), concentrated sulphuric acid (4 c.c.), and fuming sulphuric acid (2 c.c. of 10% SO_3) cooled to 0°, and, after five to ten minutes, pouring the mass on to ice, it has been found possible to obtain a *nitroclupeine*, which dissolves in dilute sodium hydroxide solution and can be precipitated by the addition of dilute acid.

When hydrolysed with 30% sulphuric acid, the nitro-compound

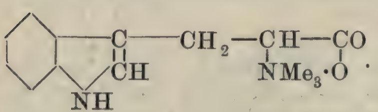
yields *nitroarginine*, $C_6H_{13}O_4N_5$, which crystallises from water, has m. p. 227—228°, and is dextrorotatory. It dissolves in dilute hydrochloric or nitric acid, and also in dilute ammonia.

A similar compound can be obtained by the action of nitric acid on *d*-arginine nitrate. J. J. S.

Hypaphorine and the Relation of this Substance to Tryptophan. Pieter van Romburgh (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 1177—1180).—The alkaloid hypaphorine, found by Greshoff (Abstr., 1891, i, 335) in the seeds of *Erythrina Hypaphorus* (the "dadap minjak" of Eastern Java), crystallises as a hydrate, efflorescing in a desiccator, m. p. 255°, $[\alpha]_D$ +91—93°. It yields a sparingly soluble nitrate.

Analysis of the anhydrous base agrees with the formula $C_{14}H_{18}O_2N_2$. When heated with strong aqueous potassium hydroxide, trimethylamine and indole are produced.

Tryptophan, treated with methyl iodide and sodium hydroxide in methyl alcohol, yields a substance, the nitrate of which closely resembles that of hypaphorine, and gives on heating with aqueous potassium hydroxide the odour of amine and indole. It is considered that hypaphorine is most probably α-trimethyl-β-indolepropiobetaine



(annexed formula) (Ellinger, Abstr., 1907, i, 737). The investigation is being continued in conjunction with Barger, who has quite recently methylated tryptophan by the method of Engeland (Abstr., 1910, i, 843), with like results. J. D. K.

Preparation of Formyl Derivatives of Morphine Alkaloids. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R-P. 233325).—The preparation of formyl derivatives of morphine alkaloids has been described previously (Abstr., 1910, i, 765); it is now found that the reaction proceeds quantitatively and at the ordinary temperature if the anhydride of another paraffinoid acid (such as acetic) is employed in conjunction with the formic acid. Details of the preparation of formylcodeine and of formyl-β-methylmorphimethine are given.

F. M. G. M.

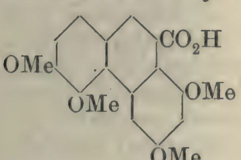
Dihydromorphine. L. Oldenberg (*Ber.*, 1911, **44**, 1829—1831).—Hitherto hydrogenised derivatives of morphine and codeine have not been obtained. By shaking aqueous morphine hydrochloride,

$$C_{17}H_{19}O_3N,HCl,3H_2O$$

(10 grams in 250 c.c. of water), with aqueous colloidal palladium (0·1 gram in 10 c.c.) saturated with hydrogen, the author has obtained *dihydromorphine*, $C_{17}H_{21}O_3N,H_2O$, in colourless needles, m. p. 155—157°. The base has the same bitter after-taste and physiological action as morphine, reacts with ferric chloride in a similar manner, and instantly reduces silver nitrate; the *hydrochloride* and the *sulphate* are described. C. S.

Constitution of Morphothebaine. II. Synthesis of the Tetramethoxyphenanthrene Derived from Morphothebaine. ROBERT PSCHORR and GEORG KNÖFFLER (*Annalen*, 1911, 382, 50—61. Compare Freund and Holthof, Abstr., 1899, i, 308; Pschorr, Abstr., 1904, i, 767; Knorr and Pschorr, 1905, i, 814).—The structural formula previously suggested (Abstr., 1910, i, 423) for morphothebaine has been confirmed by synthesising 3:4:6:8-tetramethoxyphenanthrene and proving that it is identical with the product formed from morphothebaine.

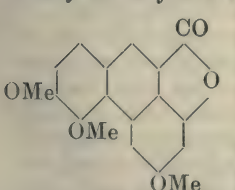
3:4-Dimethoxybenzaldehyde, hippuric acid, anhydrous sodium acetate, and acetic anhydride yield the *anhydride* of *benzoylamino-dimethoxycinnamic acid*, $C_{18}H_{15}O_4N$, which crystallises from dilute alcohol in colourless needles, m. p. 182° (corr.), and on hydrolysis with 10% sodium hydroxide solution yields dimethoxyphenylpyruvic acid and benzoic acid. The mixture of the two acids is oxidised with hydrogen peroxide in alkaline solution and then acidified and extracted with ether, when 50% of the 2:4-*dimethoxyphenylacetic acid* crystallises out on cooling to 0°. The remainder can be separated from benzoic acid by fractionation of the mixture of their ethyl esters. The acid, $C_6H_3(OMe)_2{\cdot}CH_2{\cdot}CO_2H$, crystallises in colourless needles, m. p. 113° (corr.), and its anhydrous sodium salt condenses with *o*-nitrovanillin methyl ether in the presence of acetic anhydride at 105—110°, yielding α-2′:4′-*dimethoxyphenyl*-2-*nitro*-3:4-*dimethoxycinnamic acid*, $NO_2{\cdot}C_6H_2(OMe)_2{\cdot}CH{:}C(CO_2H){\cdot}C_6H_3(OMe)_2$. The acid is purified by means of its sparingly soluble ammonium salt, and crystallises in yellow plates, m. p. 232° (corr.). When reduced with ferrous sulphate in the presence of ammonium hydroxide, the nitro-acid yields the corresponding *amino-acid*, $C_{19}H_{21}O_6N$, which crystallises from methyl alcohol in yellow cubes, m. p. 207—208°. When dissolved in methyl alcohol and dilute sulphuric acid, diazotised by the addition of *N*-sodium nitrite solution, and the resulting solution heated on the water-bath, a 30% yield of 3:4:6:8-*tetramethoxyphenanthrene*-9-*carboxylic acid* (annexed formula) is obtained. It crystallises from methyl alcohol in plates, m. p. 226° (corr.). By-products formed at the same time are: 3:4:4′-*trimethoxy*-2:2′-*oxidostilbene*-α′-*carboxylic acid*,



$$C_6H_2(OMe)_2\!<\!\begin{matrix}CH{:}C(CO_2H)\\ |\\ O\text{—}C_6H_3{\cdot}OMe\end{matrix},$$

well-developed prisms, m. p. 253°, and a product insoluble in ammonia.

The tetramethoxy-acid when heated with glacial acetic acid at 240° for twenty hours yields 3:4:6:8-tetramethoxyphenanthrene (10% yield), together with the *lactone* of 3:4:6-trimethoxy-8-hydroxyphenanthrene-9-carboxylic acid (annexed formula), m. p. 202—203°. On hydrolysis the lactone yields the corresponding acid, which crystallises from methyl alcohol in yellow prisms, m. p. 195°. With methyl sulphate, the acid yields *methyl* 3:4:6:8-*tetramethoxyphenanthrene*-9-*carboxylate*, m. p. 136—137°, which on hydrolysis gives the corresponding acid. J. J. S.



Preparation of Compounds from the Interaction of Cotarnine on Amides, Imides, or Ureides. KNOLL & Co. (D.R.-P. 232785).—The combination of cotarnine with amides, imides, or ureides yields a new class of compounds having therapeutic value.

Two *cotarnine-a-bromo*iso*valerylcarbamides* have been prepared; one is obtained by mixing molecular proportions of cotarnine and α-bromo*iso*valerylcarbamide in alcoholic solution and allowing the mixture to remain until the product separates; it forms flat prisms, m. p. 125—127°, and is decomposed by dilute mineral acids into its generators. The second compound has m. p. 105—110°, and is prepared by employing two molecules of α-bromo*iso*valerylcarbamide in aqueous solution. The preparation of the following molecular compounds of cotarnine is also recorded: *cotarnineacetamide*, m. p. 135° (about); *cotarninecarbamide*, m. p. 180°; *cotarnineurethane*, m. p. 110°; and *cotarninephthalimide*, m. p. 130°. F. M. G. M.

Solanine Extracted from Solanum sodomaeum. IV. GIUSEPPE ODDO and MARCELLO CESARIS (*Gazzetta*, 1911, 41, i, 490—534. Compare Abstr., 1905, i, 455; 1906, i, 527, 980).—Since solanine from *Solanum sodomaeum* differs in composition from that extracted from *Solanum tuberosum*, the authors term it solanine-*s*.

On analysis, after being dried in a vacuum over potassium hydroxide and paraffin, solanine-*s* gives the formula $(C_{27}H_{46}O_9N)_2,H_2O$, which is confirmed by the analysis of various normal and basic salts and other derivatives, and also by investigation of its hydrolytic products.

Carefully purified solanidine (see succeeding abstract) has the formula $C_{18}H_{31}ON$, and a study of the sugars also formed on hydrolysis of solanine shows that this change is represented thus: $(C_{27}H_{46}O_9N)_2,H_2O + H_2O + H_2 = 2C_{18}H_{31}ON + C_6H_{12}O_6$ (galactose) + $C_6H_{12}O_6$ (? dextrose) + $C_6H_{12}O_5$ (? rhamnose). In estimating the methylpentose (? rhamnose) by conversion into methylfurfuraldehyde, and weighing this in the form of its phloroglucinol derivative, higher results than were expected were obtained, and, on investigation, it was found that the presence of certain sugars, such as galactose, dimimishes, whilst that of others, namely, dextrose, increases markedly the yield of methylfurfuraldehyde.

The action of acetic anhydride on solanine-*s* yields a deca-acetyl-derivative, $C_{54}H_{82}O_{18}N_2Ac_{10}$, which yields solanine again on hydrolysis, whilst in the total products of hydrolysis of solanine, 16 atoms of hydrogen are replaceable by acetyl groups.

The action of nitrous acids on solanine-*s* (*loc. cit.*) gives a compound of the formula $C_{54}H_{86}O_{18}N_2,HNO_2,3H_2O$, which does not behave as a salt, since treatment with alkali does not yield a basic compound. When heated gently with dilute acetic acid, this compound loses all its nitrogen (it is therefore named azosolanine), yielding a compound which has not been obtained crystalline, but has the formula $C_{54}H_{86}O_{21},2H_2O$ (*oxysolanol*). Treatment of solanine with a nitrite in hot aqueous acetic acid solution results in the formation of another nitrogen-free compound, $C_{54}H_{88}O_{20},2H_2O$, which crystallises well, and is termed solanol. When heated with a dilute mineral acid, both these non-nitrogenous compounds undergo hydrolysis, yielding sugars

and other substances, which can also be obtained from solanidine; these substances are being investigated.

The following salts of solanine have been prepared: (1) Normal salts: the *hydrochloride*, $C_{54}H_{92}O_{18}N_2,2HCl$; the *sulphate*,

$$C_{54}H_{92}O_{18}N_2,H_2SO_4;$$

the o-*nitrobenzoate*, $C_{54}H_{92}O_{18}N_2,2NO_2\cdot C_6H_4\cdot CO_2H,8H_2O$; and the *picrate*, $C_{54}H_{92}O_{18}N_2,2OH\cdot C_6H_2(NO_2)_3$. (2) Basic salts: the *hydrochloride*, $C_{54}H_{92}O_{18}N_2,HCl$; the *hydrobromide*, $C_{54}H_{92}O_{18}N_2,HBr$; and the *sulphate*, $(C_{54}H_{92}O_{18}N_2)_2H_2SO_4$.

As has been indicated above, during hydrolysis solanine undergoes reduction, this being effected by the sugars formed. In fact, when heated with dextrose, solanine gives rise to a *dihydrosolanine*, $C_{54}H_{94}O_{18}N_2,H_2O$, which forms prismatic crystals, and may be the original product from which solanidine is formed.

Deca-acetylsolanine was not obtained crystalline, and may possibly be a mixture of deca- and undeca-acetyl derivatives.

Azosolanine forms tufts of faintly green, silky needles, and in the anhydrous condition has the normal molecular weight in boiling *iso*amyl alcohol. It is a neutral compound, and gives neither the nitroso-reaction with phenol and sulphuric acid nor the *iso*nitroso-reaction with a sulphuric acid solution of diphenylamine. When heated in a capillary tube it turns yellow, and contracts at 230°, blackens at 275°, and begins to melt at 280° without, however, completely fusing.

Solanol forms tufts of slender needles, which turn yellow at 210° and decompose at 240—245°. T. H. P.

Solanidine sodomaeum. V. GIUSEPPE ODDO (*Gazzetta*, 1911, 41, i, 534—552. Compare preceding abstract).—The author describes a new method of purifying solanidine. Thus obtained it has the formula $C_{18}H_{31}ON$ when dried at 105° or $3C_{18}H_{31}ON,2H_2O$ when dried under reduced pressure at the ordinary temperature. This new formula is confirmed by analysis of the various salts prepared (see below) and by a study of the hydrolysis of solanine-*s* (*loc. cit.*).

When treated with acetic anhydride, solanidine-*s* gives a diacetyl derivative, which yields the base again on hydrolysis. The formation of this compound is best explained by supposing that the oxygen exists in the molecule in the form of hydroxyl and the nitrogen in a secondary state: $OH\cdot C_{18}H_{29}\colon NH$. These functions of the oxygen and nitrogen atoms have been confirmed by treating solanidine-*s* (1 mol.) with magnesium ethyl iodide (3 mols.) in ethereal solution and measuring the amount of gas evolved:

$$OH\cdot C_{18}H_{29}\colon NH + 2MgEtI = MgI\cdot O\cdot C_{18}H_{29}\colon N\cdot MgI + 2C_2H_6;$$

2 vols. of ethane were evolved, whereas if the nitrogen atom were primary, 3 vols. should be obtained, if it were tertiary only 1 vol., due to the hydroxyl, and, if the latter were also missing, no ethane would be evolved. The iodo-magnesium compound thus obtained gives solanidine again when treated with water, and with acetyl chloride, it yields a diacetyl compound identical with that given by the action of acetic anhydride on the base.

When solanidine-*s* is treated with sodium nitrite in presence of a

little acid, a compound is obtained which is similar to that given by solanine-*s* (see preceding abstract), and is hence named azosolanidine. When treated with moderately concentrated acids, azosolanidine loses all its nitrogen, giving products which vary with the conditions of the action and are being investigated.

The formula given above for solanidine-*s* shows that this belongs to the series C_nH_{2n-4}. The lack of the six valencies necessary to make it a saturated compound is not due to the presence of double linkings in the molecule, since solanidine does not decolorise bromine in aqueous or chloroform solution, and only decolorises permanganate after some time. Solanidine-*s* must hence be regarded as a tricyclic compound.

[With EUGENIO FERRARI.]—Solanidine-*s*, separated and purified by means of its hydrochloride, crystallises from alcohol in nacreous, white scales, m. p. 197—198°, and with concentrated sulphuric acid gives a reddish-yellow coloration, which, on addition of increasing proportions of water, becomes violet, green, and colourless.

[With GIOVANNI MONETA].—The following salts of solanidine-*s* were prepared: the *basic hydrochloride*, $(C_{18}H_{31}ON)_3,2HCl$, forms silky, white needles, m. p. 302—303° (decomp.); the *hydrochloride*,

$$C_{18}H_{31}ON,HCl,$$

elongated prisms, turning yellow at about 250°, m. p. 291—292° (decomp.); the *hydrobromide*, $C_{18}H_{31}ON,HBr$, elongated prisms, becoming decidedly yellow at 270°, m. p. 282—283° (decomp.); the *o-nitrobenzoate*, $C_{18}H_{31}ON,NO_2\cdot C_6H_4\cdot CO_2H$, colourless, shining prisms, m. p. 222°; and the *picrate*, $C_{18}H_{31}ON,C_6H_3O_7N_3$, quadrangular, shining prisms, which become orange-yellow on heating, m. p. 144—145°.

[With EUGENIO FERRARI].—*Diacetylsolanidine*-s, $OAc\cdot C_{18}H_{29}\colon NAc$, was obtained only in the amorphous condition. The *iodomagnesium* compound gives solanidine when treated with water.

[With GIULIO BUZIO].—*Azosolanidine*-s form microscopic, regular, prismatic needles or rosettes of prismatic needles with a faint green tint, m. p. 260° (decomp.); its formula and the products its yields on heating with acids are being investigated. T. H. P

Action of Halogeno-Fatty Acid Halides on Esters of Malonic Acid. II. Synthesis of Tetramic Acid. ERICH BENARY (*Ber.*, 1911, 44, 1759—1765).—The substance, $C_9H_{12}O_5$, obtained as a by-product in the formation of ethyl tetrone-4-carboxylate from chloroacetyl chloride and ethyl sodiomalonate in warm ether (Abstr., 1907, i, 381) is now shown to have the constitution $C(CO_2Et)_2\colon C<\begin{matrix}O\\|\\CH_2\end{matrix}$. The amide,

$$\begin{matrix}O—\\|\\CH_2\end{matrix}>C\colon C(CO_2Et)\cdot CO\cdot NH_2,$$

obtained from it by the action of dry ammonia, is converted by an excess of boiling, alcoholic potassium hydroxide into a *potassium* salt, $C_5H_3O_4NK_2$, from which by acidification is obtained, *tetrame-*

4-*carboxylic acid*, $CO_2H\cdot C{<}\begin{array}{l}C(OH)\cdot CH_2\\ CO{-\!-\!-}NH\end{array}$, decomp. 214°. This acid does not develop a coloration with alcoholic ferric chloride, and is easily decomposed by boiling water, yielding *tetramic acid*, $OH\cdot C{<}\begin{array}{l}CH{-}CO\\ CH_2\cdot NH\end{array}$, m. p. 211° (decomp.). Tetramic acid gives a blood-red coloration with ferric chloride, has only feeble acid properties, reduces warm ammoniacal silver nitrate, and develops a violet coloration with nitrous acid, due to the *oximino*-compound, $OH\cdot N{:}C{<}\begin{array}{l}CO\cdot CH_2\\ CO\cdot NH\end{array}$, pale blue leaflets, decomp. 205°.

A by-product is not produced by the interaction of chloroacetyl chloride and methyl sodiomalonate in ether at 0°, methyl tetrone-4-carboxylate, m. p. 188—189° (decomp.), alone being produced. In a similar manner, *a*-bromopropionyl bromide and ethyl sodiomalonate (2 mols.) yield *ethyl* 1-*methyltetrone*-4-*carboxylate*,

$$CO_2Et\cdot C{<}\begin{array}{l}C(OH)\cdot CMe\\ CO{-\!-\!-}O\end{array},$$

m. p. 89—90°, which is decomposed by dilute hydrochloric acid, forming *methyltetronic acid*, $O{<}\begin{array}{l}CO{-}CH\\ CMe\cdot C\cdot OH\end{array}$, m. p. 117—119°, which develops red and violet colorations with ferric chloride and sodium nitrite respectively. C. S.

Chromoisomerism of Pyridine, Quinoline, and Acridine Salts, and its Explanation by Valency Isomerism. ARTHUR HANTZSCH (*Ber.*, 1911, 44, 1783—1828).—The existence of coloured modifications of certain pyridine, quinoline, and acridine salts has been explained at different times by the ionisation of chromophores (Decker, Abstr., 1904, ii, 702), by structural isomerism (Decker, Abstr., 1909, i, 408), or by polymerism (Hantzsch and Leupold, Abstr., 1909, ii, 198; Tinkler, Trans., 1909, 95, 921). The explanation, however, is not to be found in polymerism (compare this vol., i, 608), nor in structural isomerism in Decker's sense, but rather in the existence of chromoisomeric ammonium ions. The author quotes examples to prove that the polychromy of the salts in question, in the solid state, is independent of the nature of the anions and the cations, and in solutions is independent of the degree of association or of dissociation (in aqueous solution). The ultra-violet absorption spectra of polychromatic solutions of polychromatic salts differ greatly; even in one and the same solvent the absorption spectra vary enormously with the nature of the anion and with change of temperature or of concentration. This optical variability of polychromatic salts is in marked contrast to the optical constancy of the salts of cotarnine, the absorption spectra of which are practically identical in water, alcohol, or chloroform, and are independent of the nature of the anion. The absorption spectra show that the selective absorption of coloured ammonium salts is exclusively a property of the coloured ammonium ions, and that these organic chromophores are, in the absence of

chemical change, optically constant. It follows therefore that the solutions of the polychromatic pyridine, quinoline, *iso*quinoline, and acridine salts must, in consequence of their optical variability with the nature of the solvent or of the anion or with change of temperature or of concentration, contain, as chemically changeable chromophores, isomeric ammonium ions of different selective absorptive power; in other words, such solutions contain chromoisomeric ammonium salts. Only in certain limiting cases (as, for example, in the case of the cotarnine salts) do these solutions contain individual chromoisomerides; usually two or more chromoisomerides are present in equilibrium in the solution. The equilibrium of chromoisomeric ammonium halides is disturbed, in favour of the more strongly coloured chromoisomeride, by an increase in the associating power (or, better, by a decrease in the dissociating power) of the solvent, by an increase in the atomic weight of the halogen, and by an increase in the temperature or the concentration.

Since the solutions of a polychromatic salt (for example, 5-phenyl-10-methylacridonium sulphite) in different solvents are polychromatic, and the salt in the solid state occurs in differently coloured modifications, the polychromy is independent of a solvent and of the state of aggregation; moreover, since in solution the polychromy is referable to isomerism, the polychromy of the solid salts is also due to isomerism, not to association or polymorphism. This also follows from the genetic relation between polychromatic salt solutions and the solid salts, a relation manifested primarily by the identity of the colour of many salt solutions with that of the "solvates" (hydrates, alcoholates, chloroformates) separating therefrom. Several other phenomena are quoted to prove that the polychromy of solid pyridine, quinoline, and acridine salts is attributable to the existence of chromoisomerides.

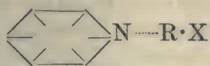
From the foregoing, the chromotropy (change of colour) of the solid salts naturally is due to chemical causes. It is a true intramolecular change of an unstable chromoisomeride into a more stable one, brought about, occasionally apparently spontaneously, more frequently by contact with a trace of a catalyst, especially with the vapours of those solvents which dissolve the chromotropic chromoisomerides with the same change of colour. The interconversions of the brown, red, yellow, and green modifications of 5-phenyl-10-methylacridonium sulphite, spontaneously or by contact with alcohol, ether, chloroform, nitrobenzene, or acetic acid, are tabulated. With regard to the number of individual chromoisomerides, it can be stated with considerable certainty in the case of the acridonium salts that the green, yellow, and red modifications are individual; all the other modifications are solid solutions or mixed salts of two, or even of all three, of these individuals.

The number of chromoisomeric salts in the pyridine, quinoline, and *iso*quinoline series cannot yet be stated with any degree of certainty, because these isomerides are much more labile than those of the acridine series, and can be isolated in the solid state only under exceptional circumstances. Apparently, however, there are two chromoisomerides in each series. One has a feeble absorbing power, and is represented by the almost colourless salts in the quinoline series, and by the quite

colourless salts of the pyridine series. The other chromoisomeride exhibits stronger selective absorption (the deep yellow to orange-red salts of the quinoline series, and the yellow salts of the pyridine series).

The salts of cotarnine and of neocotarnine also exhibit chromoisomerism (compare Salway, Trans., 1910, **97**, 1208). Cotarnine salts are especially interesting. Most of the salts with colourless anions (except the yellow iodide) are very faintly yellow in the solid state; in solution, all are intensely yellow and optically identical. This behaviour is explained by the existence of two chromoisomerides; one, feebly absorptive, is the predominating form in the solid salts, the other, strongly absorptive, is the only form stable in solution.

Chromoisomerides can be represented as valency isomerides in the light of Werner's theory of the constitution of ammonium salts. Of the four groups attached to the nitrogen atom one differs from the other three in being bound by a supplementary valency; the anion is attached to this unique group. The two chromoisomerides of the pyridine series (and in a similar manner those of the quinoline and *iso*quinoline series) can therefore be represented by the formulæ:



More stable, feebly absorptive benzenoid salt.

Strongly absorptive quinonoid salt.

In the acridine series three formulæ are possible, according as the anion is linked at positions 1, 2, or 3 in the group

$$(2)C_6H_4{<}\begin{matrix}\overset{(3)}{C}R\\ \underset{(1)}{NR}\end{matrix}{>}C_6H_4(2);$$

the yellow salts probably are benzenoid (anion in position 1), the green and the red salts quinonoid (anion in positions 2 and 3). The tendency to the formation of quinonoid instead of benzenoid salts is the greater the more unsaturated is the ring attached to the nitrogen atom; consequently, the quinonoid forms of chromoisomerides are rare in the pyridine series, occur somewhat frequently in the quinoline series, and are commonest in the acridine series.

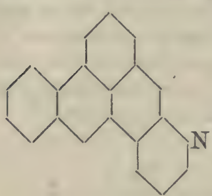
Throughout the paper numerous examples are quoted in support of the statements made. Methods are described for the preparation of yellow, green, and red modifications of the salts of the acridine series. A few new compounds, such as the yellow, orange, and green modifications of 5-*phenyl*-10-*methylacridonium thiocyanate*, are described. C. S.

Preparation of Indoxyl Derivatives. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 232780).—The action of carbonyl chloride on indoxyls (substituted or otherwise) is capable of a wide application, and leads to the production of crystalline derivatives in quantitative yield.

The *compound*, $C_6H_4{<}{N(COCl) \atop CO}{>}CH_2$, is prepared by treating an ice-

cold acid solution of indoxyl with carbonyl chloride, when the product separates out as a greyish-white, crystalline powder, m. p. 109—110°; its solution in concentrated sulphuric acid is yellow with a green fluorescence. F. M. G. M.

Action of Glycerol and Sulphuric Acid on Amino-compounds and on Compounds Free from Nitrogen Belonging to the Anthracene Group: Benzanthrone and Its Reduction Products. Observations on the Nomenclature of Complex Ring-Systems of the Anthracene Group. OSCAR BALLY and ROLAND SCHOLL (*Ber.*, 1911, **44**, 1656—1670).—The compound, $C_{20}H_{11}ON$, obtained by Bally (Abstr., 1904, i, 237) by the action of sulphuric acid and glycerol on 1-aminoanthraquinone in the absence of an oxidising agent, is now found to be 3 : 4-pyridino-1 : 9-benzanthrone (annexed formula).



With respect to the mechanism of the reaction, the authors consider that the first stage consists in the formation of β-anthraquinolinequinone (I.), which is then reduced to the anthranol derivative (II.), and finally converted by the further action of glycerol into pyridinobenzanthrone, according to the equations:

$$C_6H_4{<}^{CO}_{CO}{>}C_6H_3{\cdot}NH_2 + C_3H_8O_3 = C_6H_4{<}^{CO}_{CO}{>}C_9H_5N\text{(I.)} + 3H_2O + 2H$$

$$\text{(II.)}\ C_6H_4{<}^{CH—}_{C(OH)}{>}C_9H_5N + C_3H_8O_3 = C_{20}H_{11}ON + 3H_2O + 2H.$$

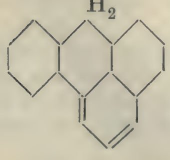
This view is supported by the fact that β-anthraquinolinequinone, on treatment with sulphuric acid and glycerol, yields pyridinobenzanthrone, and also by the behaviour of anthranol, which, when subjected to the same treatment, yields benzanthrone (Bally, *loc. cit.*). It is suggested that the formation of the latter compound is preceded by the intermediate formation of allylideneanthrone,

$$C_6H_4{<}^{C(C_3H_4)}_{CO———}{>}C_6H_4.$$

Benzanthrone may also be obtained from anthracene by the action of sulphuric action and glycerol. In this case it is probable that benzanthrene is formed as an intermediate product.

When reduced with alkaline hyposulphite or with zinc and aqueous sodium hydroxide, benzanthrone yields greenish-yellow solutions, which are considered to contain *dihydrobenzanthrone*, $C_{17}H_{12}O$.

Benzanthrene (annexed formula), prepared by distilling benzanthrone over zinc dust in a stream of hydrogen, crystallises in lustrous, pale yellow leaflets, m. p. 84°.



It gives a red coloration with sulphuric acid, and dissolves in organic solvents with a green fluorescence. In solution it is oxidised rapidly by the air to benzanthrone. The *picrate*, $C_{17}H_{12},C_6H_2(NO_2)_3{\cdot}OH$, crystallises in slender, dark red needles, m. p. 110—111°.

10-*Dibromobenzanthrene*, $C_{17}H_{10}Br_2$, is obtained by brominating benzanthrene in glacial acetic acid solution; it forms yellow crystals, m. p. 174°.

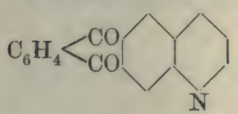
[With G. LENTZ.]—When reduced with hydriodic acid and phosphorus, benzanthrone yields (1) a *hydrocarbon*, $C_{34}H_{26}$ or $C_{34}H_{30}$, m. p. above 320°, and (2) *dihydrobenzanthrene*, $C_{17}H_{14}$, which crystallises in yellow needles, m. p. 81°, and gives green, fluorescent solutions (compare Liebermann and Roka, Abstr., 1908, i, 427); the *picrate*,

$$C_{17}H_{14},C_6H_2(NO_2)_3\cdot OH,$$

forms feather-shaped aggregates of lustrous, yellow needles, m. p. 125°.

Bromodihydrobenzanthrene, $C_{17}H_{13}Br$, prepared by brominating dihydrobenzanthrene in glacial acetic acid solution, crystallises in lustrous, colourless needles, m. p. 123°. *Dibromodihydrobenzanthrene*, $C_{17}H_{12}Br_2$, forms almost colourless needles, m. p. 157°.

2 : 3-*Pyridinoanthraquinone* [γ-*anthraquinolinequinone*] (annexed formula) is produced in small quantity in the preparation of 3 : 4-pyridino-1 : 9-benzanthrone from anthranol; it crystallises in yellow needles, m. p. 322°.



For details of the authors' proposed nomenclature of benzanthrone derivatives and allied compounds, the original must be consulted. F. B.

Quinaldinium Bases. EDUARD VONGERICHTEN and W. ROTTA (*Ber.*, 1911, 44, 1419—1422. Compare Vongerichten and Höfchen, Abstr., 1908, i, 914).—The quinaldinium base obtained by the action of *N*-sodium hydroxide solution on 2-ethylquinoline ethiodide reacts in the cold with alkali and benzoyl chloride, yielding a green oil, a warm dilute acetic acid solution of which reacts with potassium iodide and yields a pale yellow, crystalline *iodide*, $C_6H_4<\begin{matrix}NEtBzI\cdot C\colon CHBz\\ | \\ CH=\!=\!=CH\end{matrix}$, with m. p. 197°. This iodide does not give a coloration with alcoholic sodium hydroxide or with quinoline methiodide and sodium ethoxide. When boiled with concentrated hydrochloric acid in a reflux apparatus, the iodide yields benzoic acid, and on the addition of ammonia a *base*, $C_6H_4<\begin{matrix}NEt\cdot C\colon CHBz\\ | \\ CH=CH\end{matrix}$, which crystallises from alcohol in golden-yellow plates, m. p. 139°. The base dissolves in dilute acids, even acetic acid, yielding colourless solutions, but when warmed the acetic acid solution becomes deep yellow. When heated with hydrobromic acid at 200° for three hours and then made alkaline, the base yields an oil which with hydrochloric acid yields 1-ethylquinaldinium hydrochloride.

If *p*-chlorobenzoyl chloride is used instead of benzoyl chloride, the chlorinated *base*, $C_{19}H_{16}ONCl$, m. p. 187°, is obtained.

2-Methylquinoline methiodide and benzoyl chloride yield a *product*, $C_{18}H_{15}ON$, which crystallises in brilliant yellow needles, m. p. 107—108°.

The behaviour of 2-methylquinoline alkyl iodides with alkalis is thus entirely different from the reaction between quinoline alkyl iodides and alkalis, as in the latter case a rupture of the pyridine ring occurs (compare Kaufmann and Strübin, this vol., i, 321).

J. J. S.

Preparation of Thiazole Compounds of … …o-Reds" and their Derivatives. KALLE & Co. (D.R.-P. …).—The action of aldehydes and sulphur (or polysulphides) on t… …ro- or amino-substituted 2-carboxymethylthiolbenzoic acids yields thiazole derivatives, which by oxidation and closing of the ring furnish "thiazole-thioindigo" derivatives. The *product* (a thiazole derivative of 2-carboxymethylthiolbenzoic acid) prepared from benzaldehyde and 4-nitro-2-carboxymethylthiolbenzoic acid forms yellow crystals, m. p. about 250°. F. M. G. M.

***holo*- and *meri*-Quinonoid Salts of Benzidine.** WALTER MADELUNG (*Ber.*, 1911, **44**, 1674—1676).—Mainly a reply to Piccard's criticism (this vol., i, 493) of previous work of the author (this vol., i, 323). F. B.

Action of Hydrazine Hydrate on *cyclo*Hexanone. NICOLAI M. KIJNER and S. BELOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 577—582).—cyclo*Hexylidenehydrazine hydrate*, $C_6H_{10}{:}N{\cdot}NH_2,H_2O$, formed by the action of hydrazine hydrate on *cyclo*hexanone, is a colourless liquid, b. p. 107—108°/28 mm., $D_0^{19.5}$ 0·9866; on heating with dilute hydrochloric acid, it is resolved into its components, and on mixing with one or two vols. of water, it solidifies to a crystalline mass at 0°.

When reduced with absolute alcohol and sodium, the above compound yields: (1) *cyclo*hexanol; (2) cyclo*hexylhydrazine*,

$$C_6H_{11}{\cdot}NH{\cdot}NH_2,$$

m. p. 46—50°, b. p. 195·5°/758 mm., and gives a silver mirror with ammoniacal silver nitrate solution in presence of alkali; it gives the *thioureide*, $NHPh{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}C_6H_{11}$, m. p. 143—143·5°, and with pyruvic acid forms the cyclo*hexylhydrazone* of the acid,

$$CO_2H{\cdot}CMe{:}N{\cdot}NH{\cdot}C_6H_{11},$$

m. p. 110—112°; on oxidation with potassium ferricyanide it yields *cyclo*hexane.

cyclo*Hexylideneazine*, $C_6H_{10}{:}N{\cdot}N{:}C_6H_{10}$, also obtained by the interaction of hydrazine nitrate and *cyclo*hexanone, forms rhombic plates, m. p. 33·5—34°, b. p. 175°/28 mm.; the liquid remains supercooled for a long time, and has D_0^2 0·9847, n_D^{20} 1·5268.

Dicyclohexylhydrazine, $NH_2{\cdot}N(C_6H_{11})_2$, obtained by reducing the preceding compound, has b. p. 220—260°, and gives a *hydrochloride*, $C_{12}H_{25}N_2Cl$. This compound is probably formed by isomerisation of the *s*-compound, $NH{\cdot}C_6H_{11}{\cdot}NH{\cdot}C_6H_{11}$, which should be given by the reduction of the azine. T. H. P.

Relations of α-Benzaldehydephenylhydrazone to Certain Nitrogen Compounds. ROBERTO CIUSA and UGO PESTALOZZA (*Gazzetta*, 1911, **41**, i, 391—395).—The aim of the authors' experiments was to ascertain if any analogy is shown between the chemical behaviour of the more stable or α-form of benzaldehydephenylhydrazone, m. p. 156°, and that of the stable diazoaminobenzene, m. p. 96°, which may be regarded as the phenylhydrazone of nitrosobenzene.

With the latter, picric acid and picryl chloride in benzene solution give the respective intensely brown additive compounds, as is the case with phenylhydrazones of aromatic aldehydes, but these are almost

always unstable. In 96% alcohol the action of picric acid (1 mol.) on diazoaminobenzene (1 mol.) yields immediately a brown, powdery precipitate (? the picrate), which, in a few minutes, undergoes transformation into diazobenzene picrate, so that picric acid here acts in the same way as hydrochloric acid:

$$NPh\colon N\cdot NHPh + 2HCl = NPh\colon N\cdot Cl + NH_2Ph,HCl.$$

This action affords a convenient and rapid method of preparing diazobenzene picrate.

The actions of amyl nitrate and of mercuric oxide on diazoaminobenzene were studied to see if an oxidation product containing a chain of six nitrogen atoms, and analogous to that formed by benzaldehydephenylhydrazone, could be obtained:

$$2NPh\colon N\cdot NHPh \longrightarrow H_2 + NPh\colon N\cdot NPh\cdot NPh\cdot N\colon NPh.$$

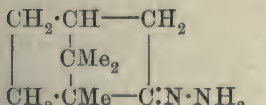
With amyl nitrate the reaction is very complex, the only product identified being diazobenzene nitrate; with mercuric oxide the latter is not reduced, the mercury salt of diazoaminobenzene being formed. This different behaviour of diazoaminobenzene from that of benzaldehydephenylhydrazone is in agreement with the acid character of the former and the feebly basic nature of the hydrazones. T. H. P.

Catalytic Decomposition of Alkylidenehydrazines as a Method of Obtaining Hydrocarbons. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 582—595).—When an alkylidenehydrazine is heated in presence of a large quantity of solid potassium hydroxide, the base decomposes as follows: $C_nH_{m-2}\colon N\cdot NH_2 = C_nH_m + N_2$, these products being the same as are obtained by the oxidation of the primary hydrazines by means of potassium ferricyanide in an alkaline solution. The alkylidenehydrazine is probably first converted by the alkali into the tautomeric diazo-form, thus:

$$C_nH_{m-2}\colon N\cdot NH_2 + KOH \longrightarrow C_nH_{m-1}\cdot N(OK)\cdot NH_2 \longrightarrow C_nH_{m-1}\cdot N\colon NH + KOH \longrightarrow C_nH_m + N_2.$$

In this way 1-methyl*cyclo*hexylidene-3-hydrazine gives a yield of 54% of methyl*cyclo*hexane, and thujylidenehydrazine, of 70% of thujane.

Camphylidenehydrazine (annexed formula), prepared by boiling camphor and hydrazine hydrate in alcoholic solution, forms a white, crystalline mass, m. p. 53—55°, $[\alpha]_D$ −40·81° (in ether), −32·74° (90% alcohol), and yields a liquid hydrate soluble in water. Its *hydrochloride*, $C_{10}H_{16}\colon N\cdot NH_2,HCl$, m. p. 180°, $[\alpha]_D$ −31·33° (water), was prepared. When hydrolysed with excess of hydrochloric acid, it is completely converted into camphor and hydrazine hydrochloride, but when 1 mol. of the acid is used per 1 mol. of the camphylidenehydrazine, in addition to camphor, a considerable quantity of camphanazine (compare Angeli and Castellana, *Atti R. Accad. Lincei*, 1905, [v], **14**, i, 669—677) is also obtained:

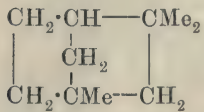


$$C_{10}H_{16}\colon N\cdot NH_2,HCl + C_{10}H_{16}O = C_{10}H_{16}\colon N\cdot N\colon C_{10}H_{16} + H_2O + HCl;$$

camphanazine has the rotations, $[\alpha]_D$ = −92·33° (benzene), −90·06° (ether), −37·27° (methyl alcohol), −19·25° (ethyl alcohol), and −14·18° (propyl alcohol).

When heated with potassium hydroxide, camphylidenehydrazine (30 grams) yields camphane (10 grams).

[With A. PROSKURJAKOFF.]—*Fenchane* (annexed formula), obtained together with fenchanazine (see below) by heating fenchylidenehydrazine (from fenchone and hydrazine hydrate) with dry potassium hydroxide, is a mobile liquid with a faint camphor-like smell, b. p. 151·5°/763 mm., D_0^{20} 0·8326, n_D^{20} 1·4463, $[\alpha]_D$ −16·53°; it does not react with permanganate, bromine, boiling fuming nitric acid, or fuming hydriodic acid in a sealed tube at 210°.



Fenchanazine, $C_{10}H_{16}:N\cdot N:C_{10}H_{16}$, forms oblique, quadrangular plates, m. p. 106°, $[\alpha]_D$ +212·9°, and is converted into fenchone and hydrazine hydrochloride on heating with concentrated hydrochloric acid.

When heated with solid potassium hydroxide, *cyclo*hexylidenehydrazine hydrate yields *cyclohexane*, $C_6H_{10}:N\cdot NH_3\cdot OH = C_6H_{12} + N_2 + H_2O$, and *cyclo*hexanol, $2C_6H_{10}:N\cdot NH_3\cdot OH = 2C_6H_{11}\cdot OH + N_2 + N_2H_4$.

T. H. P.

Quaternary Ammonium Chlorides from Diphenyl Carbamide Chloride and Pyridine or Quinoline. JOHANNES HERZOG and K. BUDY (*Ber.*, 1911, 44, 1584—1594).—Acid chlorides in presence of tertiary bases are converted into acid anhydrides by means of water or sodium carbonate. It is now found that sodium or potassium hydroxide is even more efficient at 0° in facilitating this change. The additive compound of diphenylcarbamide chloride and pyridine is thus readily converted into *diphenylcarbamic anhydride*, $(NPh_2\cdot CO)_2O$, which forms yellow crystals, m. p. 121—123°.

In addition a yellow, crystalline quaternary base, *diphenylcarbamylpyridinium hydroxide*, m. p. 189°, is obtained. This base is remarkable in being neutral, soluble in organic solvents, but insoluble in water; when hydrolysed by boiling with acetic and hydrochloric acids, diphenylcarbamide and glutaconaldehyde are formed, the latter being identified as Zincke's dianilide. Accordingly, the base has the composition: $NPh_2\cdot CO\cdot N:CH\cdot CH:CH\cdot CH:CH\cdot OH$.

Diphenylcarbamylquinolinium chloride, obtained by the interaction of the components in sunlight, forms red crystals, m. p. 135—137°. The *platinichloride* separates in yellow crystals, m. p. 232°. This reacts quite differently with sodium hydroxide; diphenylcarbamic acid is not formed, the sole product of the reaction being C-*hydroxy*-N-*diphenylcarbamyldihydroquinoline*, $C_6H_4<\begin{matrix}CH=\!=\!=CH\\N(CO\cdot NPh_2)\end{matrix}>CH\cdot OH$, a reddish-white, amorphous powder. The *ethyl ether* forms long, faintly yellow-coloured needles, m. p. 195° (quickly heated); the *methyl ether* crystallises in yellow needles, m. p. 160—162°. Both ethers on boiling with 10% hydrochloric acid are converted into diphenylcarbamylquinolinium chloride.

E. F. A.

Dehydroindigotin. III. Decomposition by means of Acids and Alkalis. LUDWIG KALB (*Ber.*, 1911, 44, 1455—1464. Compare Abstr., 1909, i, 966, 967; 1910, i, 340).—Dilute mineral acids react

with dehydroindigotin in two different ways: (1) Two molecules of water react with one of dehydroindigotin, yielding equimolecular quantities of dioxindole and isatin. (2) Two molecules of water react with two of the compound, yielding one molecule of indigotin and two of isatin. The second is the chief reaction when dehydroindigotin is boiled with water (compare O'Neill, *Chem. News*, 1892, 65, 124; Marchlewski and Radcliffe, Abstr., 1899, i, 74). The dioxindole and isatin react to form isatyde (Heller, Abstr., 1904, i, 416), a good yield of which can be obtained by shaking dehydroindigotin acetate for sixteen hours with a mixture of concentrated hydrochloric acid and water (2 : 1).

Di-isatic acid (Marchlewski and Radcliffe, *loc. cit.*), prepared by the action of sodium hydroxide solution on dehydroindigotin, is decomposed when warmed for two hours at 85° with 10% potassium hydroxide solution, yielding anthranilic acid, dioxindole, and carbon dioxide.

The formula $NH<\substack{C_6H_4 \\ CO}>C(OH)\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2H$ is suggested for di-isatic acid, and during its formation molecular rearrangement occurs. Hydrocyanoisatin when hydrolysed with alcoholic hydrochloric acid yields *ethyl hydroxyoxindole-3-carboxylate*,

$$NH<\substack{C_6H_4 \\ CO}>C(OH)\cdot CO_2Et,$$

which crystallises from water in hexagonal plates, m. p. 152°. The same ester is also formed by the action of 2*N*-sodium carbonate solution on ethyl indoxanthinate, a reaction which involves a molecular rearrangement similar to that which occurs in the formation of di-isatic acid. The reaction between alkalis and dehydroindigotin is regarded as consisting first of all in the addition of water, yielding a dihydroxyindigo-white. This by a wandering of oxygen atoms undergoes decomposition into indigotin and 2-hydroxyindoxyl-2'-carboxyanilide-2-carboxylic acid; the greater part of the latter then passes over into di-isatic acid, whilst the smaller portion is decomposed, yielding anthranilic acid, dioxindole, and carbon dioxide. J. J. S.

Indigo-Yellow. Berthold Wuth (*Chem. Zeit.*, 1911, 73, 667).—When heated with excess of benzoyl chloride, indigotin yields dibenzoylindigotin. In the presence of condensing agents, such as metals and metallic chlorides, however, the reaction proceeds differently. Only one molecule of benzoyl chloride is used, and a hitherto unknown compound of intense yellow colour is produced, crystallising from nitrobenzene in greenish-yellow needles (m. p. 275—277°). Unlike dibenzoylindigotin, it cannot be re-converted into indigotin by saponifying agents. It follows that substitution takes place at the imino-groups, and that inner condensation occurs with the formation of a new ring, thus:

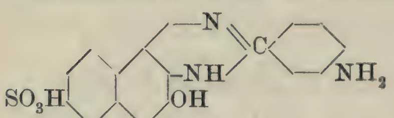
$$\begin{array}{l} C_6H_4\cdot C\!=\!=\!=\!C\!-\!C_6H_4 \\ |\qquad\ \ |\qquad\quad |\quad\ \ | \\ CO\!-\!-\!N\cdot CPh\cdot N\cdot CO \\ \qquad\qquad\ \ |\qquad\ || \end{array},$$

But whether the spare carbon valency is saturated by hydrogen or hydroxyl or by one of the indigo-nitrogens is not yet decided. Determination of the molecular weight by the boiling-point method points to the empirical formula $C_{23}H_{14}O_2N_2$.

Substitution products of indigotin, such as di-bromo-indigotin, react similarly with benzoyl chloride. Yellow condensation products are likewise obtained by replacing benzoyl chloride by its nuclear substitution products, or by benzotrichloride, benzylidene chloride, and similar substances. The compounds produced have the characteristic qualities of the vat dyes, and gives rise to greenish-yellow shades.

The above-described compound is the indigo-yellow 3G-Ciba of commerce. J. D. K.

[Preparation of 4-Hydroxy-2-*m*-aminophenyl-α-naphthiminazole-7-sulphonic Acid.] LEOPOLD CASSELLA & Co. (D.R.-P. 233939).—4-*Hydroxy*-2-m-*aminophenyl-α-naphthiminazole*-7-*sulphonic acid* (annexed formula) is prepared by the condensation of 3 : 4-diamino-β-naphthol-7-sulphonic acid with aminobenzaldehyde bisulphite; its *sodium* salt is crystalline and sparingly soluble in water. When coupled with diazotised aniline in alkaline solution, it yields a red *aminoazo*-derivative, and the properties of numerous valuable direct cotton dyes obtained when it is combined with diazo- and bisdiazo-compounds are described in the patent.



F. M. G. M.

Formation of 1-Nitroso-5-phenyl-3-pyrazolidone from Cinnamoyl Hydrazide. ERNST MUCKERMANN (*J. pr. Chem.*, 1911, [ii], 83, 513—540).—Hydrazides of monobasic unsaturated acids have been hitherto unexamined. The present work deals with *cinnamoylhydrazide*, $CHPh:CH\cdot CO\cdot NH\cdot NH_2$, m. p. 101°, which is readily obtained by boiling ethyl cinnamate with alcohol and hydrazine hydrate. It exhibits the usual reducing properties of primary acid hydrazides, yields *dicinnamoylhydrazide*, $N_2H_2(CO\cdot CH:CHPh)_2$, m. p. 247—248°, by boiling with alcoholic iodine, and forms a *hydrochloride*, m. p. 201° (decomp.), *benzylidene* compound,

$$CHPh:CH\cdot CO\cdot NH\cdot N:CHPh,$$

m. p. 180°, *benzoyl* derivative, m. p. 158—159°, and condensation *products* with acetone, $CHPh:CH\cdot CO\cdot NH\cdot N:CMe_2$, m. p. 127°, and with ethyl acetoacetate, $CHPh:CH\cdot CO\cdot NH\cdot N:CMe\cdot CH_2\cdot CO_2Et$, m. p. 125—126°. Its hydrochloride reacts with aqueous potassium cyanate to form *cinnamoylsemicarbazide*, $CHPh:CH\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2$, m. p. 161—162°. *Cinnamoylphenylthiosemicarbazide*,

$$CHPh:CH\cdot CO\cdot NH\cdot NH\cdot CS\cdot NHPh,$$

from cinnamoylhydrazide and alcoholic phenylthiocarbimide, has m. p. 146°.

Aqueous cinnamoylhydrazide hydrochloride reacts with sodium nitrite at 0° to form, not the expected azoimide, but a yellow *substance*, $C_9H_9O_2N_3$, m. p. 127—128° (decomp.), which is a nitroso-compound, but not a hydrazide on account of its strongly acid nature and absence of reducing properties. Its acid properties indicate the presence of the group $\cdot NH\cdot CO\cdot$, and the constitution, 1-*nitroso*-5-*phenyl*-3-*pyrazolidone*,

$\begin{matrix} CH_2\cdot CHPh \\ | \qquad\quad \\ CO \text{——} NH \end{matrix}\!\!>N\cdot NO$, is supported by the following evidence (compare also Knorr, Abstr., 1887, 665; von Rothenburg, *ibid.*, 1895, i, 302). Its *ammonium* salt, $C_9H_9O_2N_3,NH_3$, m. p. 147° (decomp.), obtained from the nitrosophenylpyrazolidone and 10% ammonia, is easily converted into the *silver* salt, $C_9H_8O_2N_3Ag$, m. p. 144—145°, *barium* salt, $(C_9H_8O_2N_3)_2Ba,H_2O$, greenish-blue *copper* salt,

$$(C_9H_8O_2N_3)_2Cu,2H_2O,$$

and *picrate*, $C_9H_9O_2N_3,NH_3,C_6H_2(NO_2)_3\cdot OH$, m. p. 127°; from the silver salt ethereal ethyl iodide produces 1-*nitroso*-5-*phenyl*-2-*ethyl*-3-*pyrazolidone*, m. p. 98°. The nitrosophenylpyrazolidone yields with bromine and glacial acetic acid at 0° von Rothenburg's 4:4-dibromo-3-phenyl-5-pyrazolone (Abstr., 1895, i, 686). 1-Nitroso-5-phenyl-3-pyrazolidone is converted by boiling concentrated hydrochloric acid into cinnamic acid, by cold concentrated hydrochloric acid into β-chlorodihydrocinnamic acid (?), and by boiling dilute sulphuric acid, D 1·06, into von Rothenburg's 4-oximino-3-phenyl-5-pyrazolone (*loc. cit.*).

C. S.

Preparation of 5:5-Dialkylthiobarbituric Acids. EMANUEL MERCK (D.R.-P. 234012).—The preparation of 5:5-dialkylbarbituric acids by means of carbamide has previously been described (Abstr., 1904, i, 380), and the results obtained by substituting thiocarbamide in the reaction are now recorded

Diethylthiobarbituric acid, $\begin{matrix} NH\cdot CO\cdot CEt_2 \\ | \qquad\qquad | \\ CS\cdot NH\cdot CO \end{matrix}$, yellow tablets or needles, m. p. 180°, is prepared by heating ethyl diethylmalonate with thiocarbamide in alcoholic sodium ethoxide solution at 105° with continual stirring.

Dipropylthiobarbituric acid, glistening leaflets, m. p. 154°, can be converted by removal of sulphur into *dipropylbarbituric acid*, m. p. 145°.

F. M. G. M.

Synthesis of Thiohydantoin. SHIGERU KOMATSU (*Mem. Coll. Sci. Eng.*, 1911, 3, 1—12).—The author has succeeded in preparing the previously unknown thiocarbamide form of thiohydantoin from glycine and potassium thiocyanate at 100°, using acetic anhydride as a catalyst. Thiohydantoic acid is first formed, and this loses H_2O on heating with hydrochloric acid on the water-bath, leaving the compound referred to. Similarly, *r*-alanine yields *r*-5-methylthiohydantoin.

Thiohydantoic acid, $NH_2\cdot CS\cdot NH\cdot CH_2\cdot CO_2H$, forms colourless needles, m. p. 170—171° (decomp.).

Thiohydantoin, $S:C<\begin{matrix} NH\cdot CO \\ | \\ NH\cdot CH_2 \end{matrix}$, forms colourless needles, decomposing on heating. When heated with hydrochloric acid in sealed tubes at 160°, it is decomposed into glycine, carbon dioxide, hydrogen sulphide, and ammonium chloride. It is not hydrolysed to thioglycollate like Volhard's *iso*thiocarbamide form of this hydantoin. The *potassium* salt, $SK\cdot C\begin{matrix} \nearrow N\text{—}CO \\ \qquad | \\ \searrow NH\cdot CH_2 \end{matrix}$, forms a colourless, crystalline precipitate.

2-*Methylthiohydantoin*, $SMe\cdot C\ll\begin{matrix}N\text{—}CO\\ NH\cdot CH_2\end{matrix}$, prepared by heating the potassium salt of thiohydantoin with excess of methyl iodide on the water-bath, forms colourless needles, soon darkening when kept. When fused with potassium hydroxide and acidified, it gives the odour of mercaptan.

r-α-*Methylthiohydantoic acid*, $NH_2\cdot CS\cdot NH\cdot CHMe\cdot CO_2H$, forms colourless needles, m. p. 164—165°. The *barium* salt,

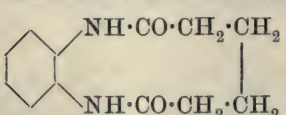
$$Ba(C_4H_7O_2N_2S)_2,H_2O,$$

is very hygroscopic, m. p. about 100°.

r-5-*Methylthiohydantoin*, $S:C<\begin{matrix}NH\cdot CO\\ NH\cdot CHMe\end{matrix}$, prepared from *r*-α-methylthiohydantoic acid, forms pearly scales, m. p. 158°. By treating the hot aqueous solution of *r*-5-methylthiohydantoin with mercuric oxide, *r*-5-methylhydantoin (Urech, Abstr., 1873, 380) is obtained.

J. D. K.

A Group of Synthetic Organic Colloids. EDGAR WEDEKIND (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 303—304).—By the action of adipyl chloride on *o*-diamines of the benzene series, amorphous substances are obtained which contain a ring of ten atoms (annexed formula). These substances are typical colloids, are insoluble in most solvents except acetic acid, and cannot be obtained in crystalline form. Colloidal solutions can be prepared by pouring acetic acid solutions into water or by triturating with potassium hydroxide solution, and afterwards treating with successive quantities of distilled water. Opalescent, milky liquids are thus obtained, which can be purified by dialysis, and exhibit all the properties of colloidal solutions. The solutions are coagulated by electrolytes, and much less readily by freezing. The possibility of obtaining these substances in colloidal form by the trituration method is supposed to be connected with their acid amide character.



H. M. D.

Behaviour of Certain Para-substituted Nitrosobenzenes towards Sulphuric Acid. EUGEN BAMBERGER and W. HAM (*Annalen*, 1911, 382, 82—128. Compare Bamberger, Büsdorf, and Sand, Abstr., 1898, i, 521).—By allowing a glacial acetic acid solution of *p*-chloronitrosobenzene to drop slowly into well stirred concentrated sulphuric acid kept at 20—24°, the chief products are 2 : 7-dichlorophenazine-5 : 10-oxide, which is insoluble in dilute alkalis and in alcohol, 4′-chloro-4-nitrosodiphenylhydroxylamine, which is soluble in dilute alkalis, unaltered *p*-chloronitrosobenzene, and 4 : 4′-dichloroazoxybenzene.

2 : 7-*Dichlorophenazine* 5 : 10-*oxide*, $C_6H_3Cl\langle\begin{matrix}N\\ O\\ N\end{matrix}\rangle C_6H_3Cl$, crystallises

from glacial acetic acid in pale golden-yellow, lustrous needles, m. p. 237·5—238° (decomp.), when rapidly heated. As a rule, it has an orange-brown colour, but this is changed to the characteristic golden-yellow after being twice treated with fuming nitric acid at the ordinary temperature. Its solution in concentrated sulphuric acid has a blood-red colour, and when reduced with stannous chloride and hydrochloric acid, it yields 2 : 7-*dichlorophenazine*,

$$C_6H_3Cl{<}\overset{N}{\underset{N}{|}}{>}C_6H_3Cl,$$

which crystallises from glacial acetic acid or xylene in glistening, lemon-yellow needles, m. p. 265·5°. Its solution in concentrated sulphuric acid is red; when moistened with concentrated hydrochloric acid it turns red, but with more acid it dissolves, yielding a yellow solution. Its alcoholic solution reacts with an alcoholic solution of silver nitrate, yielding slender, moss-green needles with a bronzy lustre. 2 : 7-Dichlorophenazine-5 : 10-oxide can be synthesised by heating *p*-chloroaniline, *p*-chloronitrobenzene, and dry sodium hydroxide for five hours at 110—120° (compare Wohl and Aue, Abstr., 1901, i, 612), but an appreciable amount of 4 : 4′-dichloroazobenzene is formed at the same time.

4′-*Chloro*-4-*nitrosodiphenylhydroxylamine*, $C_6H_4Cl\cdot N(OH)\cdot C_6H_4\cdot NO$, crystallises from acetone in greenish-yellow plates with a pronounced bronzy lustre, and has m. p. 143° (decomp.); it dissolves in alkalis and also in concentrated sulphuric acid, yielding red solutions, and when reduced with zinc dust and boiling 2*N*-ammonium chloride solution yields 4′-*chlorophenyl*-p-*phenylenediamine*,

$$C_6H_4Cl\cdot NH\cdot C_6H_4\cdot NH_2,$$

which crystallises from light petroleum in glistening, flat needles, m. p. 66·5—67°, only sparingly volatile in steam. The *hydrochloride* forms colourless, glistening crystals, and the *sulphate* is sparingly soluble. When the hydroxylamine derivative is reduced with zinc dust and hot 2*N*-hydrochloric acid, *p*-chloroaniline is also formed.

The formation of chloronitrosodiphenylhydroxylamine from *p*-chloronitrosobenzene and concentrated sulphuric acid is accompanied by the elimination of an atom of chlorine in the form of hydrogen chloride.

Under specific conditions it is possible to obtain appreciable amounts of *p*-chloronitrobenzene by the action of concentrated sulphuric acid on the corresponding nitroso-compound.

p-Bromonitrosobenzene reacts with concentrated sulphuric acid in much the same manner as its chlorinated analogue. 2 : 7-*Dibromophenazine* 5 : 10-*oxide*, $C_{12}H_6ON_2Br_2$, crystallises from glacial acetic acid or xylene in glistening, red needles, or after treatment with fuming nitric acid in golden-yellow needles, m. p. 240°, and on reduction with stannous chloride and hydrochloric acid yields 2 : 7-*dibromophenazine*, $C_{12}H_6N_2Br_2$, which crystallises from glacial acetic acid in orange-yellow or golden-yellow needles, m. p. 244·5—245°. 4′-*Bromo*-4-*nitrosodiphenylhydroxylamine*,

$$C_6H_4Br\cdot N(OH)\cdot C_6H_4\cdot NO,$$

is formed together with a dibromo-derivative, and after repeated

fractional solution in ammonium hydroxide, fractional precipitation with dilute hydrochloric acid, and crystallisation from a mixture of acetone and light petroleum, is obtained as a yellow powder with m. p. 155°. On reduction with zinc and ammonium chloride solution it yields *4′-bromophenyl-p-phenylenediamine*, $C_6H_4Br\cdot NH\cdot C_6H_4\cdot NH_2$, which crystallises from light petroleum in glistening, pale yellow needles, m. p. 75·5—76°. The *sulphate*, $2C_{12}H_{11}N_2Br,H_2SO_4$, is very sparingly soluble, and has m. p. 229°.

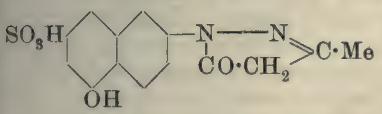
Dibromonitrosodiphenylhydroxylamine, $C_6H_4Br\cdot N(OH)\cdot C_6H_3Br\cdot NO$, has m. p. 130°. The amounts of the various products obtained from 42 grams of *p*-bromonitrosobenzene were: dibromophenazine oxide, 8·2; dibromophenazine, 0·3; bromonitrosodiphenylhydroxylamine, 5·0; dibromonitrosodiphenylhydroxylamine, 1·4; and red crystals, $C_6H_4Br\cdot NO$?, 1·5 grams.

p-Iodonitrosobenzene forms glistening, grass-green needles, m. p. 103·5—104·5° (compare *Ber.*, 1895, **28**, 249), and is accompanied by 4:4′-di-iodoazobenzene. *p*-Iodophenylhydroxylamine begins to sinter at 70°, but is not completely molten at 145°, and by-products obtained in its formation are 4:4′-di-iodoazoxybenzene, m. p. 207—208° (Gabriel, this Journ., 1877, i, 307, gives 199—199·5°), and a substance with m. p. 214—215°, which is probably an isomorphous mixture of di-iodoazobenzene and di-iodoazoxybenzene. 2:7-*Di-iodophenazine* 5:10-*oxide*, $C_{12}H_6ON_2I_2$, crystallises from xylene in glistening, brownish-yellow needles, m. p. 241° (decomp.), and when reduced yields 2:7-*di-iodophenazine*, $C_{12}H_6N_2I_2$, which crystallises in glistening, yellow needles, m. p. 235°. *4′-Iodo-4-nitrosodiphenylhydroxylamine*, $C_6H_4I\cdot N(OH)\cdot C_6H_4\cdot NO$, crystallises from acetone in glistening, greenish-yellow plates, m. p. 150—150·5° (decomp.), and is very sparingly soluble in ammonium hydroxide solution. *Di-iodonitrosodiphenylhydroxylamine*, $C_6H_4I\cdot N(OH)\cdot C_6H_3I\cdot NO$, crystallises from acetone in brownish-yellow nodules, m. p. 157° (decomp.), and is soluble in alkalis and ammonium hydroxide solution. Small amounts of lustrous, bright red plates, m. p. 188·5°, and of glistening, orange-red or yellow crystals, m. p. 240°, are also obtained by the action of concentrated sulphuric acid on *p*-iodonitrosobenzene. The amounts of products from 45 grams of *p*-iodonitrosobenzene were: *p*-iodonitrobenzene, 0·07; di-iodophenazine oxide, 7·1; iodonitrosodiphenylhydroxylamine, 2·5; di-iodonitrosodiphenylhydroxylamine, 0·4; red plates, m. p. 188·5°, 0·4; and product, m. p. 240°, 0·05 grams.

Twenty grams of *p*-nitrosotoluene when treated with concentrated sulphuric acid in the presence of glacial acetic acid gave: dimethylphenazine oxide, 4; dimethylphenazine, 0·95; *p*-azoxytoluene, 0·55; *p*-azotoluene, 0·05; mixture of azo- and azoxy-compounds, 0·5; an amorphous, dark brown powder, 6·5, and pale red powder, 2·1 grams.

2:7-*Dimethylphenazine* 5:10-*oxide*, $C_{14}H_{12}ON_2$, crystallises in glistening, pale golden-yellow needles, m. p. 204—205°. The *hydrochloride* and *sulphate* form orange-yellow, glistening needles, which are hydrolysed by water. 2:7-*Dimethylphenazine*, $C_{14}H_{12}N_2$, crystallises from alcohol in pale yellow, glistening needles, m. p. 162·5—163°, and yields a *sulphate* in the form of golden-yellow needles. J. J. S.

Preparation of Hydroxy-β-naphthylpyrazolonemonosulphonic Acids. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 233068).—When the β-naphthylpyrazolonedisulphonic acids (prepared from β-naphthylhydrazinedisulphonic acids and ethyl acetoacetate) are fused with potassium hydroxide at 160—180°, they yield the corresponding hydroxynaphthylpyrazolonemonosulphonic acids.



5′-*Hydroxy-β-naphthyl-3-methyl-5-pyrazolone-7′-sulphonic acid* (annexed formula), a colourless, crystalline powder, was thus prepared from 1-β-naphthyl-5′:7′-disulphonyl-3-methyl-5-pyrazolone; it furnishes a yellow *nitroso*-derivative.

F. M. G. M.

Azomethines derived from Phenyl*iso*oxazolone. ANDRÉ MEYER (*Compt. rend.*, 1911, **152**, 1677—1680. Compare Abstr., 1908, i, 368).—A description of new compounds analogous to that previously obtained by the condensation of phenyl*iso*oxazolone with nitrosodimethylaniline. The substances all melt with decomposition, are decomposed by alkalis, and develop a violet coloration with sulphuric acid.

4-*Diethylaminophenylimino-3-phenyl*iso*oxazolone*,

$$O<\begin{matrix}CO\cdot C{:}N\cdot C_6H_4\cdot NEt_2\\ N{=}CPh\end{matrix},$$

steel-grey prisms, m. p. 117°; the *methylethylamino*-compound forms violet needles, m. p. 143°; the *anilino*-derivative, $C_{21}H_{15}O_2N_3$, has m. p. 141—142°.

Phenyl*iso*oxazolone also condenses with nitrosopyrazoles, giving red or brown compounds of the type $O<\begin{matrix}CO\cdot C{:}N\cdot C{=\!=}CR\\ N{=}CPh\ \ CMe{=}N\end{matrix}>NR'$. Their solutions in acetic acid or alcohol are violet, but become colourless through hydrolysis.

3 : 5-*Dimethylpyrazoleimino-3′-phenyl*iso*oxazolone*, $C_{14}H_{12}O_2N_4$, m. p. 140°. 1-*Phenyl*-3 : 5-*dimethylpyrazoleimino-3′-phenyl*-iso*oxazolone*,

$$C_{19}H_{14}O_2N_4,$$

m. p. 99°. 1 : 5-*Diphenyl-3-methylpyrazoleimino-3′-phenyl*iso*oxazolone*, $C_{25}H_{18}O_2N_4$, m. p. 143—144°.

Nitrosoantipyrine condenses with phenyl*iso*oxazolone, giving the compound $O<\begin{matrix}CO\cdot C{:}N\cdot CH{-}CO\\ N{=}CPh\ \ CMe{:}N\end{matrix}>NPh$, m. p. 147—148°. The corresponding *tolyl* derivative has m. p. 152°. The two foregoing substances are somewhat analogous to purpuric acid, if the latter has the constitution ascribed to it by Slimmer and Stieglitz (Abstr., 1904, i, 634). For the purpose of comparison, alloxan was condensed with aminoantipyrine. The product having the formula

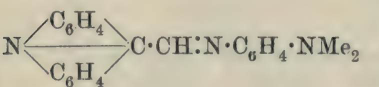
$$\begin{matrix}NMe\cdot CMe\\ NPh{-}CO\end{matrix}>C\cdot N{:}C<\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}>CO$$

resembles murexide in appearance and solubility, and in the ease with which it undergoes hydrolysis.

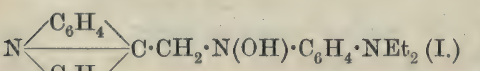
W. O. W.

Preparation of Schiff's Bases from Nitroso-compounds. A. E. PORAI-KOSCHITZ, Y. I. AUSCHKAP, and N. K. AMSLER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 518—525).—In order to test the general applicability of the empirical rule laid down by Sachs (Abstr., 1900, i, 362; 1901, i, 272; 1902, i, 118, 119) to the effect that the methylene group is capable of reacting with the nitroso-group only when it is accompanied by strongly acidic groups, such as CN, NO_2, $CO{\cdot}NH_2$, CHO, C⁚C, CO_2H, etc., the authors have investigated the reactions occurring between nitroso-derivatives and 2-methylquinoline, 2 : 6-dimethylquinoline and 5-methylacridine, which are distinguished by the great mobility of the hydrogen atoms of their methyl groups, and condense, for example, with aldehydes with much greater ease than does 2 : 4-dinitrotoluene. With 2-methylquinoline and 2 : 6-dimethylquinoline no reaction occurs under the conditions employed by Sachs, and at a higher temperature or pressure the nitroso-amines are converted into nitroso-phenols, no reaction being observed with either the methyl- or dimethyl-quinoline.

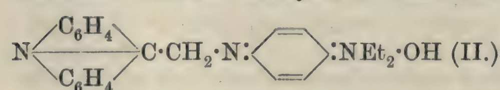
But on boiling a mixture of 5-methylacridine with *p*-nitrosodimethylaniline in alcoholic solution with a small proportion of soda, condensation occurs in a manner analogous to that observed by Sachs. The product possesses all the properties of the azomethines, and, on decomposition with hydrochloric acid, gives 5-aldehydoacridine pure and in good yield.



When *p*-nitrosodiethylaniline is used in place of *p*-nitrosodimethylaniline, 5-methylacridine yields two products: (1) the azomethine compound (annexed formula): (2) a compound, $C_{24}H_{25}ON_3$, forming orange-yellow needles, m. p. 210°.



Assuming that this compound is formed by condensation of 5-methylacridine and *p*-nitrosodiethylaniline without separation of water, that is, in the same manner as 5-methylacridine condenses with an aldehyde, it would have the structure (I); or,

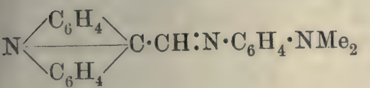


if the nitroso-compounds of amines and phenols be regarded as quinoneoximes and substituted quinoneimides, it would be represented by (II).

The orange-yellow colour of the compound agrees better with the quinonoid formula (II) than with that (I) containing no chromophore-group, since the acridine series yields coloured compounds only on the introduction of auxochrome groups in the *p*-position to the central carbon atom. Attempts to remove the elements of water from this compound by means of various dehydrating agents were unsuccessful.

The conclusion is drawn that 5-methylacridine forms an exception to Sachs' rule.

4-*Dimethylaminophenylazomethine*-5-*acridine* (annexed formula), obtained from 5-methylacridine and *p*-nitrosodimethylaniline, forms dark red crystals, m. p. 231—232°.



4-*Diethylaminophenylazomethine*-5-*acridine*, $C_{24}H_{23}N_3$, forms dark red, almost black plates, m. p. 184°, and has the normal molecular weight in boiling benzene.

5-Aldehydoacridine (compare Bernthsen and Muhlert, Abstr., 1887, 849) crystallises in shining yellow needles, m. p. 145—146°. The hydrochloride, greenish-brown prisms, and the sulphate,

$$(C_{14}H_9ON)_2,H_2SO_4,$$

small, yellowish-green needles, were prepared. T. H. P.

Carbamide Derivatives of Phenylhydrazine. Max Busch and Otto Limpach (*Ber*, 1911, 44, 1573—1583. Compare this vol. i, 334).—Monothiodicarbamides of type (I) NHR·CS·NR·NH·CO·NHR are readily obtained from *a*-thiosemicarbazides, $NHR{\cdot}CS{\cdot}NR{\cdot}NH_2$, and carbimides, whilst the isomerides of type

(II) NHR·CO·NR·NH·CS·NHR

are prepared from *a*-semicarbazides and *iso*thiocarbamides, or, less easily, from *β*-thiosemicarbazides and carbimides. The two isomerides differ especially in that the thiocarbamyl residue is only very loosely bound to the *a*-nitrogen atom of the hydrazine (type I), and is eliminated on fusion or on boiling with alcohol, whereas the *β*-thiocarbamide (type II) is completely stable. Phenylated derivatives of type (I) are not affected by boiling with alcoholic potassium hydroxide, but those of type (II) lose aniline and undergo a ring condensation to 1 : 4-diphenyltriazolone-3-thiol, $NPh<\begin{matrix}C(SK){:}N \\ CO{-}{-}NPh\end{matrix}$.

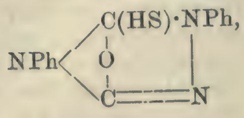
Attempts to introduce a second thiocarbimide residue into *a*-diphenylthiosemicarbazide gave *β*-diphenylthiosemicarbazide as the chief product. Addition of thiocarbimide to the *β*-nitrogen first takes place, but at the same time the group attached to the *a*-nitrogen is eliminated.

At higher temperatures phenylthiocarbimide reacts with *a*- or *β*-diphenylthiosemicarbazides, liberating hydrogen sulphide, and forming phenylanilinothiodiazolone anil.

By the action of ethyl chlorocarboxylate on *a*-diphenylthiosemicarbazide, *a-ethyl thiosemicarbazidecarboxylate* (III),

$$NHPh{\cdot}CS{\cdot}NPh{\cdot}NH{\cdot}CO_2Et,$$

is obtained, together with the isomeride (IV), $CO_2Et{\cdot}NPh{\cdot}NH{\cdot}CS{\cdot}NPh$, which is also formed in quantity from *β*-diphenylthiosemicarbazide and ethyl chlorocarboxylate. Both esters are condensed by alcoholic potassium hydroxide to triazole derivatives. The former yields 5-thiol 1 : 4-diphenyl*endo*oxydihydrotriazole (V) (annexed formula) (compare Busch and Grohmann, Abstr., 1901, i, 616); the latter gives rise to 3-thiol-1:4-diphenyltriazolone, $NPh<\begin{matrix}C(SH){:}N \\ CO{=}{=}NPh\end{matrix}$ (VI).



This triazole (V) is readily obtained directly

from ethyl phenylcarbazinate and phenylthiocarbimide in alcoholic potash. It is remarkable that some proportion of ethyl β-thiosemicarbazidecarboxylate (IV) is formed at the same time, and it is considered that in this reaction the carbethoxy-group wanders from the β- to the α-nitrogen atom of the hydrazine. Such change could not be observed in ethyl α-thiosemicarbazidecarboxylate under the influence of alcoholic potassium hydroxide.

α-Thiocarbanilido-β-carbanilidophenylhydrazine,

NHPh·CS·NPh·NH·CO·NHPh,

crystallises in colourless needles, m. p. 164°. As directly prepared it contains traces of a sulphur-free substance separating in slender, colourless needles, m. p. 214—215°, and also some 3-thiol-1:4-diphenyltriazolone, m. p. 135°, derived from the isomeric dicarbamide.

α-Carbanilido-β-thiocarbanilidophenylhydrazine,

NHPh·CO·NPh·NH·CS·NHPh,

crystallises in slender, matted needles, m. p. 178—179.

*α-Thiocarbanilido-β-carbanilido-*o*-tolylhydrazine* crystallises in colourless needles, m. p. 181°; the corresponding p-*tolylhydrazine* compound has m. p. 174°. Neither substance contains any quantity of the β-isomeride.

Ethyl βδ-diphenylthiosemicarbazide-α-carboxylate,

$NHPh·CS·NPh·NH·CO_2Et$,

from α-diphenylthiosemicarbazide, has m. p. 146° (compare Busch and Grohmann, *loc. cit.*). The isomeric *ethyl αδ-diphenylthiosemicarbazide-α-carboxylate* from the β-isomeride separates in short leaflets, m. p. 175—176°. E. F. A.

Preparation of Dialkylethylenedibarbituric Acids. ALBERT WOLFF (D.R.-P. 233968).—It is found that ethyl dialkylbutanetetracarboxylates of the general formula $CR(CO_2Et)_2·CH_2·CH_2·CR(CO_2Et)_2$ react under pressure with carbamide in the presence of alkali alcoholates.

The following compounds are described:

Ethyl dipropylbutanetetracarboxylate, plates, m. p. 103—104°.

Ethyl dibenzylbutanetetracarboxylate, m. p. 124—125°.

Diethylethylenedibarbituric acid,

$$CO{<}{}^{NH\cdot CO}_{NH\cdot CO}{>}CEt\cdot CH_2\cdot CH_2\cdot CEt{<}{}^{CO\cdot NH}_{CO\cdot NH}{>}CO,$$

colourless crystals, not melting below 300°, is prepared in 55% yield from ethyl diethylbutanetetracarboxylate, carbamide, and sodium ethoxide.

Dipropylethylenedibarbituric acid has similar properties, and is obtained in 70% yield. F. M. G. M.

Quadriurates. II. RUDOLF KOHLER (*Zeitsch. physiol. Chem.*, 1911, 72, 169—186. Compare this vol., i, 243).—A study of the solubility of uric acid in solutions of acid urates was based on the assumption that if quadriurates are formed, the solubility must be greater than in pure water, but smaller, on the other hand, if the quadriurates do not exist. Actually the solubility of uric acid decreases in presence of urates, the values agreeing with those

calculated when care is taken to prevent the absorption of carbon dioxide from the air. The conclusion is drawn that quadriurates are in reality mixtures of uric acid and acid urate. E. F. A.

Oxidation of 3- and 7-Methyluric Acids in the Presence of Ammonia. OSKAR GROHMANN (*Annalen*, 1911, **382**, 62—81. Compare Denicke, Abstr., 1906, i, 938).—The two methyl acids have been oxidised by potassium ferricyanide in the presence of concentrated ammonium hydroxide. By using 1 atom of oxygen for each molecule of acid, it was not found possible to isolate compounds corresponding with iminoallantoin; as a rule, a portion of the acid was unacted on, and another portion more completely oxidised. From 7-methyluric acid a small amount of β-methylallantoin was obtained, but the same product is formed in the absence of ammonia. The *compound*, $C_5H_{12}O_3N_6$, is formed from the two acids when $1\frac{1}{2}$ or 2 atoms of oxygen are used: $C_6H_6O_3N_4 + 2NH_3 + 2O = C_5H_{12}O_3N_6 + CO_2$. In addition a number of other products are formed, but these appear to be mainly decomposition products of the compound $C_5H_{12}O_3N_6$, which is presumably a methyl derivative of Denicke's compound, $C_4H_{10}O_3N_6$, and is to be represented as $CO{<}\begin{matrix}NMe\cdot C(NH_2)\cdot NH\cdot CO\cdot NH_2\\ NH-C(OH)\cdot NH_2\end{matrix}$ or $CO{<}\begin{matrix}NH-C(NH_2)\cdot NH\cdot CO\cdot NH_2\\ NMe\cdot C(OH)\cdot NH_2\end{matrix}$. It crystallises from warm water in glistening, six-sided prisms, decomposing at 185—187°. It does not give the murexide reaction, and is transformed into resinous substances by concentrated mineral acids. When boiled with water for some time, ammonia is evolved, and carbamide, an amorphous substance, and an ammonium salt, $C_5H_{13}O_5N_5$, are formed. The amorphous substance, when crystallised from water, yields ammonium oxalate. The *ammonium* salt, $C_5H_{13}O_5N_5$, crystallises from dilute alcohol in monoclinic, six-sided prisms, decomposing at 180—182°. The corresponding *silver* salt crystallises from water in glistening plates, decomposing at 204° after turning dark-coloured at 190°. Treatment of the ammonium salt with hydrochloric acid yields methyloxaluric acid (Breusing, *Annalen*, 1902, **323**, 167), carbamide, and ammonium chloride:

$$C_5H_{13}O_5N_5 + HCl \longrightarrow C_4H_6O_4N_2 + CON_2H_4 + NH_4Cl,$$

and attempts to synthesise the ammonium salt from oxaluric acid, carbamide, and ammonia were unsuccessful.

The compound $C_5H_{12}O_3N_6$, when warmed for fifteen minutes on the water-bath with 10% hydrochloric acid, yields methylparabanic acid, carbamide, and ammonium chloride: $C_5H_{12}O_3N_6 + H_2O + 2HCl \longrightarrow C_4H_4O_3N_2 + CON_2H_4 + NH_4Cl$, and when boiled with dilute potassium hydroxide solution the compound is completely decomposed into ammonia and oxalic acid. When, however, the compound is warmed with 2*N*-potassium hydroxide solution until dissolved, and then cooled and neutralised with 10% sulphuric acid, a *compound*, $C_5H_{10}O_5N_4$, decomposing at 185—190°, is obtained in the form of slender, felted needles.

In one experiment on the oxidation of the 7-methyl acid, a sparingly

soluble *sodium* salt, $C_5H_6O_6N_2Na_2$, was obtained from the mother liquor on the addition of sodium hydroxide.

The 3-methyl acid yields a stiff jelly with ammonium hydroxide solution, and its oxidation is most readily effected by adding a suspension of the acid in potassium ferrocyanide solution to concentrated ammonium hydroxide kept at 0°. J. J. S.

Caffolide Degradation of 3 : 7-Dimethyluric Acid and of Theobromine. HEINRICH BILTZ and ERNST TOPP (*Ber.*, 1911, 44, 1524—1532).—By the oxidation of theobromine by potassium chlorate and dilute hydrochloric acid at 40—50°, Clemm obtained "hydroxy-3 : 7-dimethyluric acid," which is converted into a more soluble isomeride by warm water (Abstr., 1898, i, 539). The former is now shown to be 3 : 7-dimethyluric acid 4 : 5-diglycol,

$$CO<\begin{matrix}NH\cdot CO\cdot C(OH)\cdot NMe \\ NMe\text{——}C(OH)\text{—}NH\end{matrix}>CO,$$

and the more soluble isomeride to be 5-hydroxy-1 : 9-dimethylhydantoylcarbamide, $NHMe\cdot CO\cdot NH\cdot CO\cdot C(OH)<\begin{matrix}NMe\cdot CO \\ CO\text{—}NH\end{matrix}$, by their degradation successively into 1-methylcaffolide and 5-hydroxy-1-methylhydantoylamide. Since 3 : 7-dimethyluric acid 4 : 5-diglycol can be obtained from 8-chlorotheobromine, which itself is prepared by the chlorination of 3 : 7-dimethyluric acid, the preceding degradation is the third example of the complete caffolide degradation of a uric acid (compare Abstr., 1910, i, 521 ; following abstract).

3 : 7-Dimethyluric acid 4 : 5-diglycol is obtained in 50—70% yield (as against Clemm's 10%) by passing a very rapid current of chlorine through a mixture of theobromine (not more than 10 grams) and glacial acetic acid containing rather more than the theoretical amount of water, the temperature being kept at about 40°. 8-Chlorotheobromine, which is conveniently obtained by rapidly chlorinating a suspension of theobromine in chloroform at the ordinary temperature, is also converted by the same treatment into 3 : 7-dimethyluric acid 4 : 5-diglycol, 8-chlorotheobromine 4 : 5-dichloride probably being formed as an intermediate product. The conversion of 3 : 7-dimethyluric acid 4 : 5-diglycol into 5-hydroxy-1 : 9-dimethylhydantoylcarbamide is simply effected by evaporating its aqueous solution on the water-bath. A mixture of the carbamide and ethyl acetate is saturated with hydrogen chloride at 0°, whereby methylamine hydrochloride and 1-*methylcaffolide*, $\begin{matrix}NH\cdot CO \\ CO\text{—}O\end{matrix}>C<\begin{matrix}NMe\cdot CO \\ CO\text{—}NH\end{matrix}$, m. p. 218—219° (decomp.), are obtained. The latter, which can be converted through its *silver* derivatives into *allo*caffeine (1 : 3 : 7-trimethylcaffolide, Abstr., 1910, i, 522), is decomposed by boiling water into carbon dioxide and 5-*hydroxy*-1-*methylhydantoylamide*, $NH_2\cdot CO\cdot C(OH)<\begin{matrix}NMe\cdot CO \\ CO\text{—}NH\end{matrix}$, m. p. 203—205° (decomp.), which is oxidised by potassium dichromate and boiling dilute sulphuric acid to methylparabanic acid. C. S.

Caffolide Degradation of 7 : 9-Diethyluric Acid 4 : 5-Diglycol. HEINRICH BILTZ and ERNST TOPP (*Ber.*, 1911, 44, 1511—1523).—7 : 9-Diethyluric acid 4 : 5-diglycol has been converted successively into the following substances by reactions similar in the main to those recorded in the case of 7 : 9-dimethyluric acid 4 : 5-diglycol (Abstr., 1910, i, 521): 5-*hydroxy*-1 : 3-*diethylhydantoylcarbamide*, $NH_2\cdot CO\cdot NH\cdot CO\cdot C(OH){<}{\begin{array}{l}NEt\cdot CO\\ CO{-}NEt\end{array}}$, m. p. 144—146° (decomp.); 1 : 3-*diethylcaffolide*, $\begin{array}{l}NH\cdot CO\\ CO{-}O\end{array}{>}C{<}\begin{array}{l}NEt\cdot CO\\ CO{-}NEt\end{array}$, m. p. 123—124°; 5-*hydroxy*-1 : 3-*diethylhydantoylamide*, $NH_2\cdot CO\cdot C(OH){<}\begin{array}{l}NEt\cdot CO\\ CO{-}NEt\end{array}$, m. p. 180—182°. The last compound forms an O-*acetyl* derivative, m. p. 157—159°, an O-*ethyl ether*, m. p. 128—129° (which is obtained better from 5-hydroxy-1 : 3-diethylhydantoylcarbamide and alcoholic hydrogen chloride), and an O-*methyl ether*, m. p. 115—117°, and is hydrolysed by aqueous barium hydroxide on the water-bath, yielding ammonia, mesoxalic acid, and *s*-diethylcarbamide; it is remarkably stable to oxidising agents, being unattacked by potassium dichromate and sulphuric acid, except after heating on the water-bath for five hours, whereby diethylparabanic acid is produced. Hydroxydiethylhydantoylamide is also unchanged by 3% or 10% hydrogen peroxide and aqueous ammonia, but, after being kept for four weeks with 30% hydrogen peroxide and a little ammonia, is converted into diethyloxamide.

5-Hydroxy-1 : 3-diethylhydantoylcarbamide reacts with warm acetone to form a *substance*, $(C_{15}H_{24}O_6N_4)_2$, m. p. 127—128° (decomp.), which yields an odour of diacetoneamine with sodium hydroxide, does not lose ammonia by treatment with hydrogen chloride, and is oxidised by potassium dichromate and sulphuric acid to 5-hydroxy-1 : 3-diethylhydantoylamide; probably it has the constitution:

$$CH_3\cdot CO\cdot CH_2\cdot CMe_2\cdot NH\cdot CO\cdot NH\cdot CO\cdot C(OH){<}\begin{array}{l}NEt\cdot CO\\ CO{-}NEt\end{array}.$$

The *silver* derivative of 1 : 3-diethylcaffolide is converted by ethyl iodide into 1 : 3 : 7-*triethylcaffolide*, $C_{11}H_{15}O_5N_3$, b. p. 155°/15 mm., which has not been obtained pure.

At 200° 1 : 3-diethylcaffolide loses carbon dioxide (1 mol.), and is converted into the *lactamide* of 5-hydroxy-1 : 3-diethylhydantoin-5-carboxylic acid, $\begin{array}{l}NH\\ CO\end{array}{>}C{<}\begin{array}{l}NEt\cdot CO\\ CO{-}NEt\end{array}$, m. p. 280—290° (decomp.); the lactamide from 1 : 3-dimethylcaffolide (*loc. cit.*) is constituted similarly.

C. S.

Preparation and Phototropy of Certain Osazones. II. MAURICE PADOA and L. SANTI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 675—680. Compare Abstr., 1910, i, 779).—*β-Benzil*-m-*tolylosazone*, $C_2Ph_2(:N\cdot NH\cdot C_6H_4Me)_2$, forms canary-yellow needles, m. p. 163°, and is feebly phototropic.

β-Piperil-m-tolylosazone, $\begin{matrix} CH_2{:}O_2{:}C_6H_3\cdot C{:}N\cdot NH\cdot C_6H_4Me \\ \vert \\ CH_2{:}O_2{:}C_6H_3\cdot C{:}N\cdot NH\cdot C_6H_4Me \end{matrix}$, forms dark yellow needles, m. p. 187°, and is phototropic.

β-Anisil-m-tolylosazone, $\begin{matrix} OMe\cdot C_6H_4\cdot C{:}N\cdot NH\cdot C_6H_4Me \\ \vert \\ OMe\cdot C_6H_4\cdot C{:}N\cdot NH\cdot C_6H_4Me \end{matrix}$, crystallises in pale yellow scales, m. p. 150·5°, and is phototropic.

β-Piperil-β-naphthylhydrazone,

$$CH_2{:}O_2{:}C_6H_3\cdot CO\cdot C(\cdot C_6H_3{:}O_2{:}CH_2){:}N\cdot NH\cdot C_{10}H_7,$$

forms a yellow, crystalline powder, m. p. 162°, and becomes darker on exposure to sunlight, but it cannot be stated with certainty that this is a phototropic change, since there is no apparent retrocession in the dark.

β-Piperil-β-naphthylosazone (*loc. cit.*) forms an *additive* compound with chloroform, $C_{36}H_{26}O_4N_4,CHCl_3$, which is obtained in yellow crystals, m. p. 80° (decomp.), and is non-phototropic.

β-Anisil-β-naphthylosazone, $\begin{matrix} OMe\cdot C_6H_4\cdot C{:}N\cdot NH\cdot C_{10}H_7 \\ \vert \\ OMe\cdot C_6H_4\cdot C{:}N\cdot NH\cdot C_{10}H_7 \end{matrix}$, forms stellar aggregates of pale yellow needles, m. p. 165—169°, and exhibits phototropy. It forms a non-phototropic *additive* compound with benzene (1 mol.), in white needles, m. p. 155—158°.

β-Anisil-o-tolylosazone forms non-phototropic, dark orange-yellow crystals, m. p. 168°.

β-Anisil-p-tolylosazone forms a pale yellow, phototropic powder, m. p. 153°, and gives a non-phototropic *additive* compound with benzene (1 mol.), m. p. 166°. T. H. P.

o-o′-Azoxybenzaldehyde. EUGEN BAMBERGER (*Ber.*, 1911, **44**, 1966—1979).—The *diethyl acetal* of *o-o′*-azoxybenzaldehyde,

$$ON_2[C_6H_4\cdot CH(OEt)_2]_2,$$

prepared by the reduction of *o*-nitrobenzaldehydediethylacetal (*p*-nitro-ωω-diethoxytoluene) with methyl alcoholic sodium methoxide, crystallises in colourless prisms, m. p. 76·5°. On hydrolysis with dilute hydrochloric acid in acetic acid solution, it yields *o-o′*-azoxybenzaldehyde.

o-o′-*Azoxybenzaldehydedimethylacetal*, $C_{18}H_{22}O_5N_2$, prepared in a similar manner to the ethyl derivative, crystallises in colourless plates, m. p. 58·5—59·5°.

When heated with aqueous sodium hydroxide, *o-o′*-azoxybenzaldehyde yields 3-hydroxy-*o*-indazylbenzoic acid. Owing to the transformation into the lactone, this has a variable m. p., depending on the method of heating. When immersed in a bath at 270°, it partly melts, then solidifies, and finally melts again at 299—300° (compare Carré, Abstr., 1906, i, 705). It yields a crystalline *hydrochloride*, which is readily hydrolysed by water. When distilled over hot zinc dust and calcium carbonate, it gives aniline and phenazine. When oxidised with chromium trioxide in glacial acetic acid solution, it yields *o-o′*-azobenzoic acid, and, when warmed with glacial acetic acid or mineral acids, it is converted into the corresponding lactone.

o-o′-Azoxybenzaldehyde, on treatment with warm glacial acetic acid, yields 3-hydroxy-*o*-indazylbenzoic acid and its lactone, together with

o-*indazylbenzoic acid*, $C_6H_4<\overset{N\text{---}}{\underset{CH}{|}}>N\cdot C_6H_4\cdot CO_2H$. The latter compound, which has also been prepared by reducing Pawlewski's *N*-*o*-nitrobenzylanthranilic acid (Abstr., 1904, i, 316) with hydrochloric acid and tin in boiling alcoholic solution, crystallises in lustrous, colourless leaves, m. p. 207·5—208·5°.

The transformation of *o*-*o'*-azoxybenzaldehyde into 3-hydroxy-*o*-indazylbenzoic acid and its lactone is also effected by exposure to light.

F. B.

Diazonium Sulphinates. MAX CLAASZ (*Ber.*, 1911, 44, 1415—1419).—Previous attempts to prepare diazonium sulphinates by von Pechmann and Hantzsch have proved unsuccessful, but it is shown that such compounds can be prepared if the sulphinic acid contains negative substituents.

o-*Nitrobenzenediazonium* o-*nitrobenzenesulphinate*,

$$NO_2\cdot C_6H_4\cdot N(\vdots N)\cdot SO_2\cdot C_6H_4\cdot NO_2,$$

prepared by adding a diazotised solution of *o*-nitroaniline to an aqueous solution of sodium *o*-nitrobenzenesulphinate (this vol., i, 437), forms yellow crystals, and has most of the properties characteristic of diazonium salts. It explodes at about 100°, and when boiled with water yields *di*-o-*nitrobenzenesulphone*, $SO_2(C_6H_4\cdot NO_2)_2$, m. p. 164°. In alcoholic solution the sulphinate has $\mu_{1000}^{18^\circ} = 1\cdot538$.

Sulphur dioxide reacts with a diazotised solution of *o*-nitroaniline, yielding *di*-o-*nitrophenylsulphohydrazide*,

$$NO_2\cdot C_6H_4\cdot NH\cdot NH\cdot SO_2\cdot C_6H_4\cdot NO_2,$$

which crystallises from ethyl alcohol in glistening, brown plates, decomposing at 153—155°. Its solutions in alkalis have a blood-red colour, and it reduces hot Fehling's solution. The same product can be obtained by condensing *o*-nitrophenylhydrazine with *o*-nitrobenzenesulphonyl chloride in alcoholic solution. When alkali is used, the products are potassium *o*-nitrobenzenesulphonate and azimidole. When oxidised with lead peroxide in the presence of acetone, the hydrazide yields *di*-o-*nitrobenzenediazosulphone*,

$$NO_2\cdot C_6H_4\cdot N\!:\!N\cdot SO_2\cdot C_6H_4\cdot NO_2,$$

a compound isomeric with the diazonium sulphinate. It crystallises from glacial acetic acid in yellow, flocculent masses, decomposing at 145°, is not explosive, and does not couple with β-naphthol.

J. J. S.

Theory of the Action of Inorganic Salts on Proteins in Solution. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1911, 9, 303—326).—The author discusses the general questions of the precipitation and coagulation of proteins. The latter term is used when a large quantity of precipitating agent is required, and it takes place even when the protein is in the non-ionic state. The precipitating agent may or may not undergo decomposition during the process.

It is suggested that the high acid and alkali combining capacities of the proteins are not to be attributed to terminal amino- and carboxylic groups, but rather to the $-CO\cdot NH-$ or $-C(OH)\!:\!N-$ groups present. In the latter form the group can react with acid in the following manner :

$-C(OH)\dot{:}N- + H^{\cdot} + Cl' = -C(OH)^{\cdot\cdot} + {}^{H}_{Cl}{>}N''-$, and with alkali as follows: $-C(OH)\dot{:}N- + Na^{\cdot} + OH' = -C(ONa)^{\cdot\cdot} + {}^{H}_{HO}{>}N''-$, and in each case only protein ions are formed. The following arguments are brought forward. (1) The compounds of proteins with acids and alkalis are excellent conductors in aqueous solution, and yet do not yield the ordinary ionic reactions, for example, a compound with hydrochloric acid does not yield chloride ions, and the equivalent conductivities at infinite dilution point to the presence of bulky organic ions. (2) Edestin is capable of displacing sodium hydroxide from its combination with hydrochloric acid, and casein can displace carbonic acid from its combination with calcium hydroxide, and yet edestin is not a strong base. The compounds do not undergo hydrolysis when diluted, and this is attributed to the fact that water does not enter into the equations given above (compare also Abstr., 1910, ii, 679). (3) Each equivalent of a mono-acid base neutralised by casein or serum-globulin yields two equivalents of protein salt, whereas if the neutralisation were effected by means of a carboxyl group each equivalent of the base would produce an equivalent of salt. (4) The osmotic pressure and depression of freezing point of casein increase in geometrical and not in arithmetical proportion on the addition of one, two, and three equivalents of a base. (5) According to Vernon (Abstr., 1904, ii, 626) the non-hydrolysed protein has nearly the same combining capacity for acid or alkali as the sum of its hydrolytic products.

It is suggested that the action of salts on the compounds of proteins with acids and alkalis is a dehydrating process, and various experiments in support of this suggestion are cited. The process of precipitation (as distinguished from coagulation) is represented by means of equations of the types:

$$-C(OK)^{\cdot\cdot} + OH\cdot NH''- + KCl = -C(OK)\cdot\underset{|}{N}{<}^{K}_{Cl} + H_2O \text{ and}$$

$$-C(OH)^{\cdot\cdot} + Cl\cdot NH''- + 2KCl = -C(OK)\cdot\underset{|}{N}KCl + 2HCl\,;$$

the product $-C(OK)\cdot\underset{|}{N}KCl$ tends to undergo hydrolysis in the presence of water, yielding $-C(OK)\cdot\underset{|}{N}HCl$, which is very sparingly soluble, and the formation of this results in precipitation. In the presence of a greater concentration of salt or of some other dehydrating agent, the hydrolysis is stopped, and hence no precipitation occurs. In the presence of still further amounts of dehydrating agents or on heating, the terminal amino- and carboxyl groups of the protein molecules react, yielding water and anhydrides which are usually insoluble, and thus coagulation is brought about. J. J. S.

Sulphur in Proteins. Thiopolypeptides. TREAT B. JOHNSON and GERALD BURNHAM (*J. Biol. Chem.*, 1911, 9, 331—332).—It is suggested that the sulphur present in proteins may be present in groups similar to those in which the oxygen is usually found, namely, $-SH$ and $-CS-NH-$. Cystein represents a compound containing the thiol group, but hitherto compounds with the $-CS\cdot NH-$ group have

not been isolated. Several compounds of this type and their derivatives have been prepared, and are being investigated. J. J. S.

The Isoelectric Point of Genuine and Denaturated Serum-Albumin. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1911, 33, 456—473).—The authors employed with small modifications the methods already described, and found that the coagulation optimum point for denaturated albumin was $0{\cdot}4 \times 10^{-5}$. The same isoelectric point was found by the method of electro-cataphoresis. The isoelectric point for genuine albumin found by the latter method was 2×10^{-5}. The electrolyte content of the mixture (which varied between $N/10$- and $N/50$-sodium acetate) had no appreciable influence. From these results it was found that the relative acidity, k_a/k_b, of albumin falls during denaturation from $7{\cdot}10^4$ to $3{\cdot}10^3$. S. B. S.

Hydrolysis of Sodium "Iodeigon." ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, 72, 374—379. Compare Mosse and Neuberg, Abstr., 1903, ii, 496).—When sodium "iodeigon" is boiled with barium hydroxide solution, 96·5% of the iodine is eliminated as hydriodic acid within the first 4·5 hours. Non-crystallisable resins are also obtained, but no indication of di-iodotyrosine and no *o*-iodobenzoic acid. The behaviour of "iodeigon" towards hydrolysing agents is thus different from that of iodo-albacid (this vol., i, 203) and iodo-glidin (*ibid.*, 372). J. J. S.

Analysis of the Products of Hydrolysis of Wheat Gliadin. THOMAS B. OSBORNE and H. H. GUEST (*J. Biol. Chem.*, 1911, 9, 425—438).—Owing to improved methods, it appeared desirable to undertake a fresh investigation of gliadin, a protein much used in nutrition experiments. Analytical results are given in full, in reference to the partition of nitrogen, the yield of amino-acids, and these results are compared with those in other proteins. The total yield of amino-acids amounted to 83·54% of the original protein, and the deficit is probably due to losses incurred in estimating those amino-acids which are obtained from their esters. W. D. H.

A New Decomposition Product of Keratin which gives Millon's Reaction. ROSS A. GORTNER (*J. Biol. Chem.*, 1911, 9, 355—357).—A positive reaction with Millon's reagent in a protein is generally taken as evidence of the presence of tyrosine. It is, however, shown that in a melano-protein prepared from black wool after hydrolysis yielded, not only tyrosine, but there was in the mother liquor a substance which still gave Millon's reaction with great intensity. This substance is evidently an aromatic phenolic material, but it has not yet been identified. W. D. H.

The Laws of Enzyme Action. P. VON GRÜTZNER [with W. WALDSCHMIDT] (*Pflüger's Archiv*, 1911, 141, 63—117).—Experiments showed that, under similar conditions, the amount of protein or gelatin digested is in direct linear proportion to the quantity of enzyme present. This applies to experiments with pepsin, trypsin, and ptyalin when the time occupied is short; if prolonged, this law no

longer holds, but the rate of change conforms to Schütz' law, and this finally ceases to apply. The retardation of change is greater in the case of high concentration of enzyme.

When equal amounts of change are allowed to take place, the velocity of change is in direct proportion to the amount of enzyme. If the substrate be increased, there ensues in the case of pepsin (less in the case of ptyalin) a reduction in the rate of change. On the other hand, under similar conditions, the higher concentrations of trypsin digest at a proportionately greater rate than the lower concentrations.

The view is expressed that no single law can be applied to the whole course of enzymic change. H. B. H.

The Digestibility of White of Egg as Influenced by the Temperature at which it is Coagulated. PHILIP FRANK (*J. Biol. Chem.*, 1911, **9**, 463—470).—The Mett tube method is regarded as untrustworthy, owing to the inclusion of air bubbles, the setting of the albumin in the tubes in uneven layers, and to the fact that the digestibility of the egg-white varies according to the temperature used in producing coagulation. The last factor is regarded as very important and is treated at length. W. D. H.

The Identity of Pepsin and Rennet. AGNES ELLEN PORTER (*J. Physiol.*, 1911, **42**, 389—401).—Several commercial preparations of rennet were found to be milk curdling, but non-peptic, or were antipeptic. The antipeptic material is indifferent to rennet, and can be removed by dialysis. A rennet zymoid occurred spontaneously, which was indifferent to pepsin. The results are in favour of the view that the two enzymes are not identical. W. D. H.

Nucleases. II. PHŒBUS A. LEVENE and FLORENTIN MEDIGRECEANU (*J. Biol. Chem.*, 1911, **9**, 389—402).—That the final oxidation, etc., of purine bases is due to the graded action of specific enzymes has been established by Walter Jones and Schittenhelm, and is confirmed by the present experiments. The so-called nucleases really include three groups of enzymes. These may be designated: (1) *Nucleinases*, which resolve the molecule into mono-nucleotides; such an enzyme occurs in all organs, and in pancreatic juice, but not in gastric juice. (2) *Nucleotidases*, which liberate phosphoric acid, leaving the carbohydrate base complexes (nucleosides) intact. They are present in all organs, juices, and in intestinal juice, but are absent from gastric and pancreatic juices. There are probably specific enzymes to deal with each nucleotide. (3) *Nucleosidases* are the enzymes which cleave hydrolytically the nucleosides into their components, the carbohydrate ribose, and their bases of the purine or pyrimidine groups. These are absent in all the digestive juices and in the plasma of the pancreas, but are present in the plasmata of most other organs. W. D. H.

The Inhibition of the Action of Invertase. ANSELM ERIKSSON (*Zeitsch. physiol. Chem.*, 1911, **72**, 313—338).—Invertase can be removed wholly or in part from its solutions by charcoal. The removal, and in this way the inhibition, of its action is greater if

the charcoal is added before the mixing of the enzyme and substrate than if it is added after the mixture has occurred. Time and temperature are other factors. Normal serum also inhibits the activity of invertase, and the order in which it is added is a factor, although not so great a one, as in the case of charcoal. Inhibiting substances occur also in the invertase solution itself; they are not destroyed by boiling, they diffuse very slowly through a membrane, and are not to any great extent absorbed by charcoal. W. D. H.

Synthesis of Mercuriated α-Anilino-fatty Acids. WALTER SCHOELLER, WALTHER SCHRAUTH, and PAUL GOLDACKER (*Ber.*, 1911, 44, 1300—1312). In order to determine the influence exerted by the amino-group on the introduction of mercury into the benzene nucleus, the authors have investigated the action of mercuric acetate on the ethyl esters of α-anilinoacetic acid and its homologues. It is found that the introduction of mercury proceeds more easily as the series is ascended. Whilst ethyl α-anilinoacetate forms only a monosubstitution product, the propionic ester reacts with mercuric acetate in equal molecular proportions, yielding a mixture of the mono- and di-substitution products. In the case of the butyric and *iso*valeric esters, only disubstituted products of the type

$$C_6H_3(Hg\cdot OAc)_2\cdot NH\cdot CHR\cdot CO_2Et$$

could be obtained.

Ethyl o-*acetoxymercurianilinoacetate*, $OAc\cdot Hg\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO_2Et$, prepared by the addition of aqueous mercuric acetate to a methyl alcoholic solution of ethyl anilinoacetate, forms small, tabular crystals, m. p. 132° (corr.), with previous softening at 129° (corr.). When shaken with bromine in aqueous potassium bromide, it yields *ethyl* o-*bromoanilinoacetate*, which crystallises in white needles, m. p. 82—83°; the corresponding o-*iodo*-compound forms greyish-white leaflets, m. p. 86—87°.

Ethyl o-*chloromercurianilinoacetate*, $HgCl\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO_2Et$, is obtained by the action of sodium chloride on the preceding acetoxymercuri-ester in aqueous alcoholic solution; it crystallises in needles or rhombic plates, m. p. 152·5° (corr.), with previous sintering at 150·5° (corr.). *Ethyl* o-*bromomercurianilinoacetate* forms rhombic plates, which sinter at 144°, and have m. p. 147·5° (corr.); the corresponding *iodo*-ester crystallises in lustrous leaflets, m. p. 139—140° (corr.), with previous sintering at 137—138° (corr.).

o-*Hydroxymercurianilinoacetic anhydride*, $C_6H_4{<}{\begin{matrix}NH-CH_2\\ Hg\cdot O\cdot CO\end{matrix}}$, prepared by hydrolysing the acetoxymercuri-ester with sodium hydroxide and acidifying the resulting solution, decomposes at 228° (corr.); the *copper* salt, $(HO\cdot Hg\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO_2)_2Cu$, decomposes at 193—197° (corr.); the *lead*, *iron*, *calcium*, *silver*, *mercury*, and *platinum* salts are also mentioned.

Ethyl α-acetoxymercurianilinopropionate is obtained together with a small quantity of the diacetoxymercuri-ester by the reaction of equal molecular quantities of mercuric acetate and ethyl α-anilinopropionate, but since it could not be obtained free from the accompanying dimercuri-ester, it was converted by the action of sodium chloride into

ethyl α-chloromercurianilinopropionate, $HgCl\cdot C_6H_4\cdot NH\cdot CHMe\cdot CO_2Et$; this crystallises in microscopic needles, m. p. 165·5° (corr.).

Ethyl α-diacetoxymercurianilinopropionate,

$$C_6H_3(Hg\cdot OAc)_2\cdot NH\cdot CHMe\cdot CO_2Et,$$

which crystallises in leaflets, m. p. 186° (corr.), is prepared by the interaction of mercuric acetate (2 mols.) and ethyl α-anilinopropionate (1 mol.) in aqueous methyl-alcoholic solution; a less soluble, apparently polymeric form is produced simultaneously. When treated with sodium chloride, it yields *ethyl α-dichloromercurianilinopropionate*, $C_{11}H_{13}O_2NCl_2Hg_2$, which forms small needles, m. p. 131° (corr.), with previous softening at 128°; the corresponding *dibromomercuri*-ester crystallises in needles, m. p. 128·5° (corr.), with previous softening.

α-Dihydroxymercurianilinopropionic anhydride,

$$OH\cdot Hg\cdot C_6H_3{<}\begin{matrix}NH-CHMe\\ \quad\ \ |\\ Hg\cdot O\cdot CO\end{matrix},$$

prepared from the diacetoxymercuri-ester by hydrolysis with aqueous sodium hydroxide, decomposes at 223° (corr.).

Ethyl α-diacetoxymercurianilinobutyrate,

$$C_6H_3(Hg\cdot OAc)_2\cdot NH\cdot CHEt\cdot CO_2Et,$$

prepared from ethyl α-anilinobutyrate in the usual manner, crystallises in stout rods, sintering at 150°, m. p. 154·5° (corr.). On treatment with sodium chloride, it yields *ethyl α-dichloromercurianilinobutyrate*, $C_{12}H_{15}O_2NCl_2Hg_2$, which forms slender needles, m. p. 127° (corr.), with previous softening at 125° (corr.); the corresponding *dibromo*-ester crystallises in needles, softening at 125° (corr.), m. p. 127° (corr.); the *di-iodo*-ester has m. p. 120° (corr.).

α-Dihydroxymercurianilinobutyric anhydride,

$$OH\cdot Hg\cdot C_6H_3{<}\begin{matrix}NH-CHEt\\ \quad\ \ |\\ Hg\cdot O\cdot CO\end{matrix},$$

is obtained by hydrolysing the preceding diacetoxymercuri-ester; when heated, it becomes yellowish-brown at 200°, and decomposes at 209° (corr.); it readily takes up water on exposure to air, forming $C_{10}H_{13}O_4NHg_2$.

Ethyl α-diacetoxymercurianilinoisovalerate,

$$C_6H_3(Hg\cdot OAc)_2\cdot NH\cdot CHPr^{\beta}\cdot CO_2Et,$$

prepare from ethyl α-anilino*iso*valerate and mercuric acetate, crystallises in tufts or stellar aggregates of needles, m. p. 126° (corr.).

Ethyl α-dichloromercurianilinoisovalerate, $C_{13}H_{17}O_2NCl_2Hg_2$, forms microscopic rods, m. p. 122° (corr.); the corresponding *dibromomercuri*-ester occurs in two forms: a granular, sandy, amorphous modification, which decomposes at 215° without melting, and is insoluble in ethyl acetate; and a soluble form crystallising in tufts of white needles, m. p. 135° (corr.); the *di-iodomercuri*-ester forms yellow needles, m. p. 129° (corr.).

α-Dihydroxymercurianilinoisovaleric anhydride,

$$OH\cdot Hg\cdot C_6H_3{<}\begin{matrix}NH-CHPr^{\beta}\\ \quad\ \ |\\ Hg\cdot O\cdot CO\end{matrix},$$

decomposes at 226° (corr.), and readily takes up water on exposure to air. F. B.

Organic Chemistry.

The Grignard Reaction in its Application to Dihalogen Compounds. I. JULIUS VON BRAUN and WLADISLAUS SOBECKI (*Ber.*, 1911, **44**, 1918—1931. Compare Abstr., 1907, i, 997; Zelinsky and Gutt, *ibid.*, 676; Grignard and Vignon, *ibid.*, 689).—The authors find that the interaction of magnesium with $\alpha\delta$-dibromobutane, $\alpha\epsilon$-dibromopentane, $\alpha\eta$-dibromoheptane, or $\alpha\kappa$-di-iododecane yields only about half of the theoretical amount of the normal magnesium compound, $MgX\cdot[CH_2]_n\cdot MgX$, the remainder of the dihalogen derivative being converted into a mixture of magnesium compounds of the general formula $MgX\cdot[C_nH_{2n}]_x\cdot MgX$.

No evidence of the formation of cyclic or unsaturated hydrocarbons, or of magnesium compounds of the type $MgX\cdot[CH_2]_n\cdot Br$, was obtained.

The magnesium compound of $\alpha\delta$-dibromobutane reacts with carbon dioxide, yielding *cyclo*pentanone, sebacic acid, and dodecamethylenedicarboxylic acid.

When treated with water, the magnesium compound of $\alpha\epsilon$-dibromopentane gave pentane, decane, pentadecane, and eicosane, together with still higher homologues.

The magnesium compound of $\alpha\eta$-dibromoheptane, when similarly treated, yields a mixture of hydrocarbons, from which heptane and tetradecane were isolated; it reacts with carbon dioxide, yielding a mixture of acids, $CO_2H\cdot[CH_2]_{7n}\cdot CO_2H$, from which azelaic acid is separated by boiling it with water.

By decomposing the magnesium compound of $\alpha\kappa$-di-iododecane with water, decane, eicosane and tetracontane were obtained; the action of carbon dioxide yields a mixture of the acids $CO_2H\cdot[CH_2]_{10n}\cdot CO_2H$, from which decane-$\alpha\kappa$-dicarboxylic acid may be readily separated by extraction with hot water.

The magnesium compound of $\alpha\epsilon$-dibromopentane reacts with acetone, yielding the following compounds: (1) β-methylheptan-β-ol (Muset, Abstr., 1907, i, 374), the formation of which takes place according to the scheme: $COMe_2 + MgBr\cdot[CH_2]_5\cdot MgBr \longrightarrow MgBr\cdot O\cdot CMe_2\cdot[CH_2]_5\cdot MgBr \xrightarrow{H_2O} OH\cdot CMe_2\cdot[CH_2]_5\cdot H$; (2) a *liquid*, $C_{11}H_{22}O$, b. p. 107—109°/14 mm., D_4^{20} 0·8467, n_D 1·45512, having an odour resembling citronellol, and consisting probably of a mixture of the unsaturated alcohols, $OH\cdot CMe_2\cdot[CH_2]_5\cdot CMe{:}CH_2$ and

$$OH\cdot CMe_2\cdot[CH_2]_4\cdot CH{:}CMe_2;$$

(3) *βι-dimethylnonan-βι-diol*, $OH\cdot CMe_2\cdot[CH_2]_5\cdot CMe_2\cdot OH$, which has b. p. 135—145°/12 mm., and readily solidifies to a white, crystalline mass, m. p. 77°.

βι-Dibromo-βι-dimethylnonane, $C_{11}H_{22}Br_2$, prepared by the action of hydrobromic acid on the preceding glycol in glacial acetic acid solution, is a viscid oil, which loses hydrogen bromide when heated with pyridine, and is converted into the unsaturated *hydrocarbon*,

$C_{11}H_{20}$, b. p. 180—185°, D_4^{20} 0·7759, n_D 1·4504; the latter compound yields an oily *tetrabromide*, and probably consists of a mixture of two or three structural isomerides.

By the interaction of trioxymethylene with the magnesium compound of $\alpha\epsilon$-dibromopentane, the authors hoped to find a ready means of passing from the pentamethylene group to the heptamethylene group:

$$MgBr\cdot[CH_2]_5\cdot MgBr + 2CH_2O \longrightarrow OH\cdot CH_2\cdot[CH_2]_5\cdot CH_2\cdot OH.$$

Their hopes were, however, not realised, partly on account of the difficulty with which trioxymethylene enters into reaction, and partly because of the difficulty of isolating the easily soluble heptane-$\alpha\eta$-glycol from the reaction product. F. B.

Attempted Preparation of Methylene Derivatives. HERMANN STAUDINGER and OTTO KUPFER (*Ber.*, 1911, **44**, 2194—2197).—The authors have attempted in various ways to decompose substances such as tetrachloroethylene, tetraphenylethylene, benzyl chloride, benzylidene chloride, chlorodiphenylmethane, and ethyl orthoformate, in the hope of obtaining compounds containing a bivalent carbon atom attached to two other elements or to two carbon atoms. In every case, however, the result is negative, the methylene derivative, if formed temporarily, being converted by polymerisation into an ethylene derivative or by additive reactions into a derivative of methane. C. S.

Reduction and Oxidation by Catalysis. PAUL SABATIER (*Ber.*, 1911, **44**, 1984—2001).—A lecture before the German Chemical Society, summarising the author's experiments on the catalytic reduction of organic compounds by passing their vapours, mixed with hydrogen, through metallic tubes, especially nickel, at a temperature of about 180°. At 250° the same metals bring about a catalytic oxidation, for example, of alcohols to aldehydes or ketones. E. F. A.

Cyanopinacolin and Some Compounds Derived From It. OSKAR WIDMAN and ERIK WAHLBERG (*Ber.*, 1911, **44**, 2065—2071).—By the interaction of equivalent quantities of bromine and pinacolin, a mixture of bromo- and dibromo-pinacolin is obtained.

ω-Bromopinacolin is a colourless liquid, which attacks the skin and eyes, b. p. 77—78°/15 mm., 184—188°/760 mm., D^{17} 1·33.

ω-Dibromopinacolin has m. p. 75° (compare Scholl and Weil, *Chem. Zeit.*, 1899, **23**, 189).

The monobromide reacts with potassium cyanide, yielding *ω-cyanopinacolin* (tert.-*valerylacetonitrile*); this forms colourless, well-shaped crystals with many faces, and centimetre-long prisms, m. p. 68—68·5°. The *potassium* salt, $CMe_3\cdot C(OK)\colon CH\cdot CN$, crystallises in colourless tablets.

The *hydrochloride* of tert.-*valerylacetimino-ether*,

$$CMe_3\cdot CO\cdot CH_2\cdot C(OEt)\colon NH,HCl,$$

prepared by the action of hydrogen chloride on cyanopinacolin dissolved in a mixture of alcohol and ether, crystallises in large four- or six-sided prisms, m. p. 126—127° (decomp.) when quickly heated, or

m. p. 131° (slowly heated). The *platinichloride* forms long, yellow needles, m. p. 135°.

tert.-*Valerylacetamide*, obtained on heating the imino-ether hydro chloride, crystallises in large, glistening plates, m. p. 95°.

Phthaliminopinacolin, prepared by heating bromopinacolin with potassium phthalimide in alcohol, crystallises in lustrous, stout, four-sided prisms with hemihedric faces, m. p. 102°.

Pinacolylphthalamic acid crystallises in well formed four- or six-sided plates or prisms, m. p. 132°.

Pinacolylamine, $CMe_3\cdot CO\cdot CH_2\cdot NH_2$, is obtained as *hydrochloride* on evaporating the phthalamic acid with hydrochloric acid; it is deliquescent. The base was characterised by warming with potassium cyanate and conversion into 2-*hydroxy*-5-tert.-*butylglyoxaline*, $CMe_3\cdot C\Big\langle\begin{matrix}CH-N \\ \qquad\ \| \\ NH\cdot C\cdot OH\end{matrix}$, which separates in needles, m. p. 277—278°.

E. F. A.

Effect of Heating Mixed Esters of Carbonic Acid. Alfred Einhorn and Leo Rothlauf (*Annalen*, 1911, **382**, 237—265. Compare Einhorn, Abstr., 1909, i, 568).—The velocity with which mixed carbonic esters lose carbon dioxide and yield phenolic ethers depends largely on the nature of the alkyl group present. With common alkyl groups such as methyl and ethyl, the decomposition takes place slowly, but becomes more rapid when strongly basic substituents are present in the alkyl group. Attention is drawn to the fact that numerous isolated examples of this type of decomposition are recorded in chemical literature. The formation of esters of organic acids by the action of ethyl chlorocarbonate on sodium salts (R. and W. Otto, Abstr., 1888, 813; 1891, 288) is a reaction of a similar type; a mixed anhydride, $R\cdot CO\cdot O\cdot CO\cdot OEt$, is formed as an intermediate product, and decomposes into carbon dioxide and the ester. Similarly, the mixed anhydrides, formed by the action of the salts of aromatic acids on diphenylcarbamide chloride in the presence of pyridine, lose carbon dioxide and yield diphenylated acid amides (Herzog, Abstr., 1909, i, 568; Herzog and Hancu, 1908, i, 268). Acid anhydrides with catalysts yield ketones (Mailhe, Abstr., 1909, i, 692; compare Senderens, *ibid.*, 287), and by heating benzyl and *p*-nitrobenzyl esters of chlorocarbonic acid, benzyl chloride and *p*-nitrobenzyl chloride are formed (Thiele and Dent, Abstr., 1898, i, 15; compare also F. Hofmann, *Zeitsch. angew. Chem.*, 1908, **21**, 1986). Similarly, aldehydes when heated with carbonyl chloride yield carbon dioxide and the corresponding chloride.

Guaiacyl methyl carbonate, $OMe\cdot C_6H_4\cdot O\cdot CO_2Me$, obtained by the action of methyl chlorocarbonate on guaiacol in the presence of pyridine, has b. p. 132—134°/16 mm., and when heated at 234° and then at 218° yields guaiacol and catechol dimethyl ether, together with guaiacyl carbonate and unaltered guaiacyl methyl carbonate. Guaiacyl ethyl carbonate has b. p. 265°, and when boiled for seven days in a reflux apparatus yields guaiacol and its ethyl ether.

Resorcinyl diethyl dicarbonate, $C_6H_4(O\cdot CO_2Et)_2$, has b. p. 174—176°/19 mm. or 270—288° under atmospheric pressure (Wallach

gives 298—302°). When boiled for twenty-eight hours it yields resorcinol mono- and di-ethyl ethers, and an insoluble product, probably a high molecular resorcinyl carbonate. *Resorcinyl ethyl carbonate*, $OH\cdot C_6H_4\cdot O\cdot CO_2Et$, when freed from resorcinol by digesting with water, crystallises from light petroleum in plates, m. p. 52—53°, b. p. 170—173°/11 mm. or 274° under atmospheric pressure, and when boiled for seven hours yields resorcinol monoethyl ether, resorcinyl carbonate, and resorcinol. By boiling β-naphthyl methyl carbonate for 46·5 hours, β-naphthol, its carbonate, and methyl ethers are obtained. Aryl-diethylaminoethyl carbonates can be prepared by the action of diethylaminoethanol on phenyl chlorocarbonates (D.R.-P. 118537) in benzene solution.

Guaiacyl chlorocarbonate (Barral and Morel, Abstr., 1899, i, 802) is best prepared by the action of a benzene solution of carbonyl chloride on guaiacol in the presence of quinoline, and with diethylaminoethanol yields guaiacyl diethylaminoethyl carbonate, the *hydrobromide* of which, $C_{14}H_{21}O_4N,HBr$, crystallises from acetone in rhombohedra, m. p. 99—100°.

Diethylaminoethylguaiacol, $OMe\cdot C_6H_4\cdot O\cdot C_2H_4\cdot NEt_2$, obtained by distilling guaiacyl diethylaminoethyl carbonate once or twice under reduced pressure, is a colourless oil, b. p. 148—150°/10 mm. The *hydrobromide* has m. p. 127—128°. *Thymyl diethylaminoethyl carbonate*, $C_6H_3MePr^{\beta}\cdot O\cdot CO_2\cdot C_2H_4\cdot NEt_2$, obtained from *thymyl chlorocarbonate*, b. p. 122—124°/25 mm., is a yellow oil; the *hydrobromide* crystallises from alcohol in slender needles, m. p. 160°, and the *citrate*, $C_{23}H_{35}O_{10}N$, in microscopic crystals, m. p. 90—95°. When distilled twice under reduced pressure, the base gives a quantitative yield of *diethylaminoethylthymol*, $C_6H_3MePr^{\beta}\cdot O\cdot C_2H_4\cdot NEt_2$, as a liquid with b. p. 126°/18 mm. The *citrate*, $C_{22}H_{35}O_8N$, crystallises from alcohol in prisms, m. p. 142—143°.

β-Naphthyl chlorocarbonate, $C_{10}H_7\cdot O\cdot COCl$, has b. p. 150—152°/9 mm., and crystallises from light petroleum in slender, yellow needles, m. p. 65—66°. *β-Naphthyl diethylaminoethyl carbonate*,

$$C_{10}H_7\cdot O\cdot CO_2\cdot C_2H_4\cdot NEt_2,$$

is a basic oil; its *hydrochloride*, $C_{17}H_{21}O_3N,HCl$, crystallises from acetone in colourless needles, m. p. 141°, and when the base is distilled twice under reduced pressure the *diethylaminoethyl ether* of β-naphthol, $C_{10}H_7\cdot O\cdot C_2H_4\cdot NEt_2$, is obtained as a yellow oil, b. p. 202°/18 mm.; its *hydrochloride*, $C_{16}H_{21}ON,HCl$, crystallises from a mixture of alcohol and ether in small plates, m. p. 138—139°. The *chlorocarbonate* derived from ethyl salicylate, $COCl\cdot O\cdot C_6H_4\cdot CO_2Et$, is a colourless oil, b. p. 144°/12 mm., and reacts with diethylaminoethanol, yielding the *ethyl* ester, $CO_2Et\cdot C_6H_4\cdot O\cdot CO_2\cdot C_2H_4\cdot NEt_2$, as a yellow oil, the *hydrobromide* of which forms minute crystals from acetone, m. p. 106—108°. *Ethyl diethylaminoethylsalicylate*,

$$CO_2Et\cdot C_6H_4\cdot O\cdot C_2H_4\cdot NEt_2,$$

has b. p. 179—180°/10 mm., and its *hydrochloride* crystallises from ethyl acetate in needles, m. p. 112°. The *methyl* ester,

$$CO_2Me\cdot C_6H_4\cdot O\cdot CO_2\cdot C_2H_4\cdot NEt_2,$$

yields a *hydrobromide*, which crystallises from a mixture of acetone and ether in needles, m. p. 127—130°.

The *chlorocarbonate* from methyl *p*-hydroxybenzoate,

$$CO_2Me\cdot C_6H_4\cdot O\cdot COCl,$$

has b. p. 144°/13 mm., and crystallises from light petroleum in yellow needles, m. p. 58°.

Methyl p-*diethylaminoethylcarbonatobenzoate*,

$$CO_2Me\cdot C_6H_4\cdot O\cdot CO_2\cdot C_2H_4\cdot NEt_2,$$

is a yellow oil; its *hydrochloride* crystallises from absolute alcohol in glistening needles, m. p. 133—134° (decomp.), and decomposes in the presence of water, yielding carbon dioxide, diethylaminoethanol hydrochloride, and methyl-*p*-hydroxybenzoate.

Methyl p-*diethylaminoethoxybenzoate*, $CO_2Me\cdot C_6H_4\cdot O\cdot C_2H_4\cdot NEt_2$, has b. p. 186—189°/15 mm.; its *hydrochloride* crystallises from ethyl acetate in thin, glistening plates, m. p. 147°.

Ethyl diethylaminoethyl carbonate, $OEt\cdot CO\cdot O\cdot C_2H_4\cdot NEt_2$, obtained from ethyl chlorocarbonate and diethylaminoethanol, is a colourless oil, b. p. 91—94°/10 mm.; the *citrate*, $C_{15}H_{27}O_{10}N$, crystallises from ethyl acetate in needles, m. p. 93—98°. When the base is boiled in a reflux apparatus, the temperature registered is 207°, but falls and finally remains constant at 172°, the products of decomposition being ethyl alcohol, ethyl carbonate, and diethylaminoethanol.

Menthyl diethylaminoethyl carbonate, $C_{10}H_{19}\cdot O\cdot CO\cdot O\cdot C_2H_4\cdot NEt_2$, obtained from *menthyl chlorocarbonate*, b. p. 105—106°/12 mm., and diethylaminoethanol, is a colourless liquid, b. p. 179—180°/9 mm.; its *hydrochloride*, $C_{17}H_{33}O_3N,HCl$, crystallises from ethyl acetate in prismatic needles, m. p. 142°. When the base is boiled for some hours, the temperature falls from 215° to 204°, and menthol, menthyl carbonate, m. p. 105°, diethylaminoethanol, and its carbonate are formed. J. J. S.

Esters and Amides of the Phosphoric Acids. II. Attempts to Prepare Substances Allied to the Lecithins. KURT LANGHELD (*Ber.*, 1911, **44**, 2076—2087. Compare Abstr., 1910, i, 536).—Esters of metaphosphoric acid unite with alcohols to form esters of orthophosphoric acid of the type $OR\cdot PO(OR')\cdot OH$. At the ordinary temperature the addition of alcohol takes place quantitatively in the course of four to five days, but in the case of solid alcohols, such as sugar, combination takes place very slowly. The behaviour of ethyl metaphosphate towards ammonia and its derivatives has also been studied. It is found that ammonia and primary amines yield derivatives of iminophosphoric acid, $NH[PO(OEt)\cdot OH]_2$ and

$$NR[PO(OEt)\cdot OH]_2,$$

whilst secondary amines and primary bases containing strongly acid groups in the molecule (carbamide and aminodicarboxylic acids) are converted into derivatives of ethyl aminophosphoric acid of the types $NRR'\cdot PO(OEt)\cdot OH$ and $NHR\cdot PO(OEt)\cdot OH$ respectively; tertiary bases yield salts having the constitution $\begin{matrix}O\\ |\\ NR_3\end{matrix}\!\!>PO\cdot OEt$.

When shaken with ethyl metaphosphate in chloroform solution at the ordinary temperature, aminomonocarboxylic acids give rise to readily soluble derivatives of diethyl iminopyrophosphate, whereas aminodicarboxylic acids remain unchanged. Serine unites with three

molecules of ethyl metaphosphate, of which two are easily removed by boiling with water and lead carbonate. It is suggested that the separation of amino-acids might be effected by utilising these differences in their behaviour towards the ester.

Details of the preparation of ethyl metaphosphate from silver metaphosphate and ethyl iodide, and also by the interaction of phosphoric oxide and diethyl ether, are given. The ester may also be obtained by heating diethyl hydrogen orthophosphate under diminished pressure at 80°; at higher temperatures, triethyl orthophosphate is produced. Diethyl hydrogen orthophosphate is readily prepared by the interaction of ethyl metaphosphate and alcohol in molecular proportions at the ordinary temperature.

When metaphosphoric acid is heated with alcohol and the resulting solution treated with water and barium hydroxide, barium ethyl orthophosphate, $C_2H_5O_4PBa,H_2O$, and barium diethyl orthophosphate, $Ba(C_4H_{10}O_4P)_2$, are produced; the separation of these two salts is accomplished by taking advantage of the greater solubility of the latter in aqueous alcohol.

Ethyl metaphosphate reacts with water at the ordinary temperature to form *diethyl dihydrogen pyrophosphate*, which gives an amorphous *barium* salt, $C_4H_{10}O_7PBa$.

Molecular quantities of ethyl metaphosphate and ethylene chlorohydrin, when kept for three to four days at the ordinary temperature, yield *ethyl chloroethyl hydrogen orthophosphate*, which was isolated in the form of its *barium* salt, $Ba(C_4H_9O_4ClP)_2$. When ethyl metaphosphate is heated on the water-bath with excess of ethylene chlorohydrin, a mixture of diethyl hydrogen orthophosphate and ethyl chloroethyl hydrogen orthophosphate is produced.

Benzyl alcohol reacts with ethyl metaphosphate in boiling chloroform solution, yielding benzyl ethyl ether and dibenzyl ether, together with *benzyl dihydrogen phosphate* and *ethyl benzyl hydrogen phosphate*, the reaction taking place according to one or both of the following schemes:

I. $OEt{\cdot}PO(O{\cdot}C_7H_7){\cdot}OH + C_7H_7{\cdot}OH = PO(O{\cdot}C_7H_7)(OH)_2 + C_7H_7{\cdot}OEt$.

II. (*a*) $PO_2{\cdot}OEt + C_7H_7{\cdot}OH = PO_2{\cdot}OH + C_7H_7{\cdot}OEt$.

(*b*) $PO_2{\cdot}OH + C_7H_7{\cdot}OH = PO(O{\cdot}C_7H_7)(OH)_2$.

The two esters were isolated in the form of their *barium* salts, $C_7H_7O_4PBa,2H_2O$ and $Ba(C_9H_{12}O_4P)_2$.

Ethyl choline phosphate is obtained as a hygroscopic, glassy mass by treating ethyl chloroethyl hydrogen orthophosphate with trimethylamine in alcoholic solution; the yellow, amorphous *platinichloride* was analysed.

Glycerolphosphoric acid is prepared by heating ethyl metaphosphate with excess of glycerol; the *barium* salt has the composition $C_3H_6O_6PBa,1\frac{1}{2}H_2O$.

When allyl iodide, diluted with chloroform, is shaken with equal molecular quantities of silver metaphosphate and ethylene chlorohydrin, allyl phosphate and *allyl chloroethyl hydrogen orthophosphate*, are produced. The *barium* salt of the last-named compound has the composition $Ba(C_5H_9O_4ClP)_2$.

The *compounds* of ethyl metaphosphate with ammonia, $C_4H_{19}O_6N_3P_2$,

ethylamine, $C_{10}H_{31}O_6N_3P_2$, diethylamine, $C_{10}H_{27}O_3N_2P$, and with triethylamine, $C_{18}H_{20}O_3NP$, are all syrups, which solidify to glasses when kept in a desiccator under diminished pressure.

The *compound* with carbamide, $C_3H_9O_4N_2P$, is hydrolysed when boiled with water into carbamide and ethyl dihydrogen phosphate.

Aspartic acid and glutamic acid react slowly with ethyl metaphosphate in boiling chloroform solution, yielding glassy *substances* of the composition $C_6H_{12}O_7NP$ and $C_7H_{14}O_7NP$ respectively.

The *compounds* with alanine, $C_7H_{17}O_8NP_2$, valine, $C_9H_{21}O_8NP_2$, and leucine, $C_{10}H_{23}O_8NP_2$, were obtained in the form of glassy masses, which are decomposed when boiled with water into ethyl dihydrogen phosphate, phosphoric acid, and the corresponding amino-acid. The leucine derivative gives with diethylamine a *salt*, $C_{22}H_{56}O_8N_4P_2$, containing three molecules of diethylamine.

The *compound* of ethyl metaphosphate with serine has the composition $C_9H_{22}O_{12}NP_3$. F. B.

αβ-Dimethyl-lævulic Acid. Richard Willstätter and Alessandro Brossa (*Ber.*, 1911, **44**, 2191—2194).—*αβ-Dimethyl-laevulic acid*, COMe·CHMe·CHMe·CO_2H, required for comparative purposes in connexion with the degradation of phytol, has been obtained from alcoholic sodium ethoxide and equimolecular quantities of methyl α-bromopropionate and methyl methylacetoacetate, whereby mixtures of the methyl and ethyl esters of αβ-dimethylsuccinic acid and of acetyldimethylsuccinic acid are obtained. The hydrolysis of the latter by 8% barium hydroxide yields a mixture of αβ-dimethylsuccinic acid and the acid required. αβ-Dimethyl-lævulic acid has b. p. 120°/5 mm., 145°/12 mm., and D_4^0 1·112, and forms an *ethyl* ester, b. p. 90°/9 mm., D_4^0 0·999, p-*nitrophenylhydrazone*, m. p. 121—123° (decomp.), and *anhydride*, b. p. 114°/16 mm., 235—237°/727 mm., D_4^0 1·084. C. S.

Ethyl *tert.*-Valerylacetate. Erik Wahlberg (*Ber.*, 1911, **44**, 2071—2076).—Attempts to prepare ethyl *tert.*-valerylacetate, CMe_3·CO·CH_2·CO_2Et, by the interaction of magnesium *tert.*-butyl iodide and ethyl cyanoacetate, and also by the removal of carbon monoxide from ethyl trimethylacetylpyruvate, proved fruitless. The ester is obtained in small yield by the condensation of pinacolin with ethyl carbonate by means of sodium ethoxide or sodamide. It is best prepared by heating an aqueous solution of *tert.*-valerylacetiminoether hydrochloride at 50—60° (see this vol., i, 702). It is a colourless liquid, b. p. 96—97°/15 mm., D_4^{18} 0·967, giving an intense violet coloration with ferric chloride. When hydrolysed with aqueous potassium hydroxide it yields tert.-*valerylacetic acid*,

CMe_3·CO·CH_2·CO_2H,

which has m. p. 47—49°, and decomposes at 100° into pinacolin and carbon dioxide.

Ethyl tert.-*valerylmethylacetate* or *ethyl αγγγ-tetramethylacetoacetate*, CMe_3·CO·CHMe·CO_2Et, prepared by the successive action of sodium ethoxide and methyl iodide on the above ester, is an oil, b. p. 93—94°/15 mm., D_4^{18} 0·955. The corresponding *acid*,

CMe_3·CO·CHMe·CO_2H,

crystallises in small, lustrous plates, which have m. p. 100—101°, and simultaneously decompose into carbon dioxide and ethyl *tert.*-butyl ketone.

1-*Phenyl*-3-tert.-*butyl-5-pyrazolone*, $C_{13}H_{16}ON_2$, prepared by the interaction of phenylhydrazine and ethyl *tert.*-valerylacetate, crystallises from benzene in large leaves, m. p. 110·5—111·5°, and when oxidised with ferric chloride in alcoholic solution yields *bisphenyl*-tert.-*butylpyrazolone*, $C_{26}H_{30}O_2N_4$, m. p. above 290°.

1-*Phenyl-4-methyl*-3-tert.-*butyl-5-pyrazolone*, $C_{14}H_{18}ON_2$, prepared from phenylhydrazine and ethyl αγγγ-tetramethylacetoacetate, has m. p. 114·5—115·5°.

Ethyl ααγγγ-*pentamethylacetoacetate*, $CMe_3·CO·CMe_2·CO_2Et$, obtained from ethyl tetramethylacetoacetate by the successive action of sodium ethoxide and methyl iodide, has b. p. 98·5—99°/15 mm., and on hydrolysis with dilute sulphuric acid yields pentamethylacetone. When heated with phenylhydrazine, it gives 1-*phenyl*-4 : 4-*dimethyl*-3-tert.-*butyl-5-pyrazolone* in an impure condition, m. p. 107—108°.

F. B.

Ketoglutaric Acids and the Acid-aldehydes of the Succinic Series. EDMOND E. BLAISE (*Compt. rend.*, 1911, **153**, 71—73).—When ethyl oxalopyrotartrate is saturated with hydrogen bromide at 0°, and allowed to remain for some weeks, crystals are obtained, together with a viscous liquid. The latter is esterified and distilled, when three fractions are obtained : (1) A liquid, b. p. 143—145°/15 mm., which consists principally of an *ester* of the above-mentioned crystalline substance; on hydrolysis it forms the *lactone*, $\begin{matrix}CHMe·CH\\ | \\ CO\text{———}O\end{matrix}\!\!>\!C·CO_2Et$, and when treated with barium hydroxide it yields the *aldehyde*, $CO_2Et·CHMe·CH_2·CHO$, b. p. 89—90°/18 mm. The latter forms a *semicarbazone*, m. p. 110·5°, a p-*nitrophenylhydrazone*, m. p. 89°, an *oxime*, b. p. 137—138°/16 mm., and an *azine*, $CHMe\!<\!\begin{matrix}CH{=}N\\ CH_2·CO\end{matrix}\!>\!NH$, m. p. 66°, b. p. 134—136°/18 mm. (2) The foregoing aldehyde. (3) An *ethoxylactone*, $\begin{matrix}CHMe\text{—}CH_2\\ | \\ CO·CH(OEt)\end{matrix}\!\!>\!O$, having b. p. 101°/18 mm.

The *acid-aldehyde*, $CO_2H·CHMe·CH_2·CHO$, has b. p. 139—140°/12·5 mm.; the *semicarbazone*, m. p. 195°; the *oxime*, m. p. 77°; the p-*nitrophenylhydrazone* has m. p. 198°; the *phenylhydrazone*, m. p. 71—72°, and on distillation forms an *azine*, m. p. 42°, b. p. 183—185°/12 mm.

W. O. W.

Action of Organo-magnesium Compounds on Methyl Acetylpyrotartrate. PHILIPPE BARBIER and RÉNÉ LOCQUIN (*Bull. Soc. chim.*, 1911, [iv], **9**, 717—722).—An attempt was made to prepare acids of the type $OH·CRR'·CH(CO_2H)·CH_2·CO_2H$ by the action of magnesium alkyl bromides on methyl acetylpyrotartrate,

$$CO_2Me·CH_2·CMeAc·CO_2Me.$$

The esters alone could be obtained, however, the only products on saponification being pyrotartaric acid and the corresponding ketone, R·COMe.

The authors tried magnesium *iso*butyl bromide and magnesium phenyl bromide, and obtained from these respectively the compounds $CHMe_2\cdot CH_2\cdot CMe(OH)\cdot CMe(CO_2Me)\cdot CH_2\cdot CO_2Me$, an oily liquid, b. p. 157—158°/14 mm., and

$$OH\cdot CMePh\cdot CMe(CO_2Me)\cdot CH_2\cdot CO_2Me,$$

a light-coloured, odourless oil, which decomposed on distillation even under reduced pressure.

The experiments furnish a new method of preparing ketones containing the group COMe. W. G.

A New Method of Obtaining Glycuronic Acid. ADOLF JOLLES (*Biochem. Zeitsch.*, 1911, **34**, 242—247 *).—The acid was obtained by the oxidation of 2% dextrose solution by hydrogen peroxide. After destruction of the excess of the latter by platinum-black, the acid was precipitated by basic lead acetate. It was identified by the isolation of the *p*-bromophenylhydrazine derivative, and by oxidation to saccharic acid. S. B. S.

Lactonisation of α-Ketonic Esters. HENRI GAULT (*Compt. rend.*, 1911, **153**, 107—110).—α-Ketonic esters of mono- and of di-carboxylic acids under the influence of amines, sulphuric acid, or, best of all, sodium ethoxide undergo condensation in accordance with the scheme: $R\cdot CO\cdot CO_2Et + CH_2R'\cdot CO\cdot CO_2Et \longrightarrow$

$$CO_2Et\cdot CR(OH)\cdot CHR'\cdot CO\cdot CO_2Et \longrightarrow CO_2Et\cdot CR{<}\begin{matrix}O\text{—}CO\\ CR'{:}C\cdot OH\end{matrix}.$$

The products are viscous liquids, which cannot be distilled without decomposition, dissolve in alkali carbonates or hydrogen carbonates, develop violet-red colorations with ferric chloride, and form acyl derivatives; with the exception of the substance obtained from ethyl pyruvate, they do not react in the ketonic forms; thus ethyl pyruvate yields *ethyl α-keto-γ-valerolactone-γ-carboxylate*,

$$CO_2Et\cdot CMe{<}\begin{matrix}O\text{—}CO\\ CH{:}C\cdot OH\end{matrix}$$

(*phenylhydrazone*, m. p. 120—121°; *semicarbazone*, m. p. 220°), whilst ethyl α-ketosuccinate, α-ketoglutarate, and α-ketoadipate respectively yield substances in which R is $CH_2\cdot CO_2Et$, $CH_2\cdot CH_2\cdot CO_2Et$, and $CH_2\cdot CH_2\cdot CH_2\cdot CO_2Et$ respectively, and R′ is CO_2Et, $CH_2\cdot CO_2Et$, and $CH_2\cdot CH_2\cdot CO_2Et$ respectively. C. S.

Chemical Action of Light. II. G. INGHILLERI (*Zeitsch. physiol. Chem.*, 1911, **73**, 144—151).—The formation of a sugar, m. p. 98°, by the action of light on a mixture of 40% formaldehyde solution and crystallised oxalic acid in sealed tubes has been confirmed (compare this vol., i, 354). Formaldehyde itself (40% solution) when similarly exposed yields a yellow, syrupy liquid, but when mixed with water and then exposed to sunlight a yellow syrup, methyl alcohol, and formic acid are formed, the two latter probably by the action of the alkali of the glass on the formaldehyde. A mixture of methyl alcohol and formaldehyde (40%) under similar conditions yields methyl formate. Tubes containing glycerol, oxalic acid, and a little water

* and *Monatsh.*, 1911, **33**, 623—629.

gave a yellow oil containing glyceryl monobutyrate, together with a liquid containing butyric acid. J. J. S.

Viscose from Cellulose and from Starch. HERMANN OST, F. WESTHOFF, and L. GESSNER (*Annalen*, 1911, **382**, 340—360).—Starch yields a viscose similar to that obtained from cellulose, but it is more stable, and allows the process of "ripening" to be studied more readily. To obtain the viscose, 10 grams of potato starch are suspended in 20—25 c.c. of carbon disulphide in a stoppered bottle, the mixture is shaken, and at least 2 mols. of sodium hydroxide are added at once in the form of 10—20% aqueous solution. After some hours, a yellow jelly is obtained, which can be drawn out in the form of slender threads. This xanthate dissolves in water to a viscous liquid, from which alcohol or saturated saline solutions precipitate the xanthate as a leather-like mass. Mineral acids and concentrated acetic acid yield starch, carbon disulphide, and hydrogen sulphide. When kept, the viscose becomes thinner, it "ripens," but, even after months, coagulation is not observable. Very dilute alkali and an excess of very concentrated (50%) alkali do not yield a viscose.

The products, after purification by repeated solution in water and precipitation by alcohol, were analysed, the sodium was estimated as sodium sulphate, the sulphur estimated by oxidation by Carius' method, as Cross's method of oxidation with hypochlorite gave low results, and the starch estimated by decomposing with acid, hydrolysing to dextrose, and estimating this by means of Fehling's solution.

The composition of different samples varied appreciably, mainly owing to hydrolysis, which takes place during solution and precipitation. In most cases for 1 mol. of starch, 1·35—1·25 atoms of S and 1·3—1·2 atoms of Na were found. The formula suggested for the xanthate is $(ONa\cdot C_6H_8O_3\cdot O\cdot CS\cdot SNa)_n$, but owing to hydrolysis, which can take place according to the two equations:

(1) $(ONa\cdot C_6H_8O_3\cdot OCS_2Na)_n + nH_2O = (C_6H_9O_4\cdot OS_2Na)_n + nNaOH$, and (2) $(C_6H_9O_4\cdot OCS_2Na)_n + n/2\text{-}H_2O = (C_{12}H_{19}O_9\cdot OCS_2Na)_{n/2} + n/2\text{-}CS_2 + n/2\text{-}NaOH$, the percentages of sulphur and sodium are low.

During the process of ripening, the viscose becomes less and less viscous; for example, a specimen purified by three precipitations with alcohol, when dissolved in water and examined in an Engler's viscometer at 20°, had a viscosity of 130, but this fell within twenty-five days to 9. The ripening is accompanied by hydrolysis similar to that which occurs during purification, but to a greater extent. After keeping crude viscose for twelve days and then purifying by three precipitations with alcohol, the number of atoms of sulphur and sodium compared with 1 mol. of starch had fallen to 0·34 and 0·29 respectively, whereas the numbers for the fresh viscose were 1·77 and 1·82. The diminution in the viscosity is not due to this hydrolysis, but to the action of the alkali on the starch, that is, to a diminution of the value *n*. This is supported by the fact that soluble starch and dextrins of high molecular weight yield comparatively mobile xanthates.

Viscose from cellulose also undergoes hydrolysis during purification and ripening. During the latter process its viscosity first diminishes

and then increases again, the final increase being due to the colloidal separation of free cellulose.

The cellulose deposited from an old specimen of viscose by means of hydrochloric acid is apparently identical with the cellulose obtained from alkali cellulose, and its composition is practically that of cellulose, provided the specimens are thoroughly dehydrated at 120—125°.

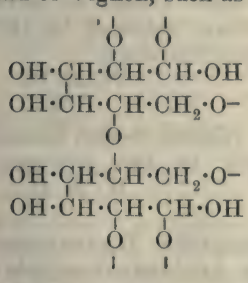
An erythrodextrin obtained by the action of malt extract on starch paste at 70° has practically no reducing properties, and differs but little from starch in composition. J. J. S.

Acid Hydrolysis of Starch Granules. CHESTER B. DURYEA (*J. Soc. Chem. Ind.*, 1911, 30, 789—790).—It has been demonstrated experimentally that maltose is formed quite early in the hydrolysis of maize starch granules by hydrochloric acid; in fact, it is not improbable that it is an initial product of the hydrolysis of starch. It would also appear that the production of maltose is accompanied by a general simplification of the molecular condition of the carbohydrates composing the granules; in other words, the production of each successive molecule of maltose leads to the formation of a simpler dextrin. W. H. G.

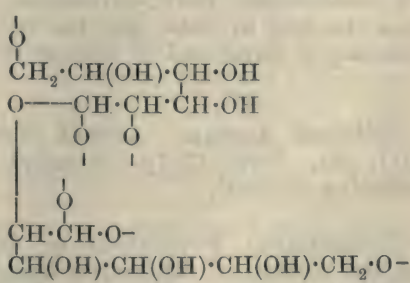
Observations on Cotton and Nitrated Cotton. HENRY DE MOSENTHAL (*J. Soc. Chem. Ind.*, 1911, 30, 782—786).—Attempts to dialyse solutions of nitrocellulose in acetone, making use of the bladder of the sturgeon and also parchment paper, have led to the conclusion that, contrary to the author's earlier statements (*ibid.*, 1904, 23, 292; 1907, 26, 443), nitrocellulose does not dialyse. Further, solutions of nitrated cotton in acetone do not give any indication of a pressure in a Pfeffer osmometer with various septa.

The absorption spectra of a number of solutions of cellulose nitrates and acetates were investigated; in all cases a continuous spectrum was observed, which showed a shortening in the ultra-violet progressing with the concentration; it may be assumed therefore that the cellulose group absorbs ultra-violet light.

The author inclines to the view that the dextro-cellulose of cotton is an aliphatic compound of a polysaccharide character, most suitably represented by open formulæ derived from the ring formulæ of Green and of Vignon, such as:



and



The latter formula seems preferable, since the monose groups are connected by acetal linkings only, which would account for the ease

with which cellulose is hydrolysed and also the formation of a large number of celluloses and hydrocelluloses by the addition of water.

W. H. G.

Acetylation of Cotton Cellulose. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1911, **24**, 1256—1260).—It has been shown previously (compare Abstr., 1910, i, 224) that the cellulose acetates obtained by the processes of Bayer (D.R.-P. 159524) and of Lederer (D.R.-P. 163316) are acetates of hydrocelluloses. The present communication contains the results of experiments performed with the object of ascertaining at which stage of the process the hydrolysis of the cellulose occurs. It is found that the first product of the interaction of cotton cellulose with acetic anhydride and acetic acid in the presence of sulphuric acid is an acetate of a cellulose derivative capable of reducing Fehling's solution (hydrocellulose). As the reaction proceeds, however, cellulose acetates are formed, which, when hydrolysed, yield cellulose derivatives incapable of reducing boiling alkaline copper solutions; in agreement with this, it is found that the product first formed in the Lederer process (acetylation of hydrocellulose) consists of acetates of a cellulose derivative which does not reduce Fehling's solution. Towards the end of the reaction, acetates of hydrocelluloses again appear, and, as already stated, the final product consists almost solely of acetates of a hydrocellulose.

Evidence is also brought forward to show that the acetylation of the hydrocellulose initially produced proceeds at a far greater rate than the formation of the hydrocellulose itself from the cotton cellulose.

It is evident from the results now recorded that the hydrolysis which takes place during acetylation cannot be regarded as a tertiary process, as stated by Jentgen (compare this vol., i, 115).

W. H. G.

Cellulose. Hydrocellulose. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1911, **24**, 1260—1262. Compare this vol., i, 115).—Polemical. A reply to Jentgen (this vol., i, 355). W. H. G.

Cellulose Acetate. HERMANN OST (*Zeitsch. angew. Chem.*, 1911, **24**, 1304—1306, 1307).—Historical. The author claims to have been the first to show that the cellulose acetate obtained by the processes of Bayer and of Lederer is a cellulose triacetate.

W. H. G.

Cellulose Acetate. ARTHUR EICHENGRÜN (*Zeitsch. angew. Chem.*, 1911, **24**, 1306—1307).—Polemical. A reply to Ost (compare preceding abstract). W. H. G.

Thioamides: Formation of Thiopolypeptide Derivatives by the Action of Hydrogen Sulphide on Aminoacetonitrile. TREAT B. JOHNSON and GERALD BURNHAM (*J. Biol. Chem.*, 1911, **9**, 449—462).—Aminoacetonitrile reacts normally with hydrogen sulphide

at the ordinary temperature, giving the unknown thioamide of glycine, which, however, was not isolated. It is very unstable, and decomposes spontaneously in alcoholic solution to the thiopolypeptide derivative, *thioglycylglycinethioamide*, $NH_2 \cdot CH_2 \cdot CS \cdot NH \cdot CH_2 \cdot CS \cdot NH_2$. In part this thioamide undergoes an inner condensation with loss of ammonia, forming a *dithiopiperazine*, $NH<\begin{matrix}CH_2 \cdot CS\\CS \cdot CH_2\end{matrix}>NH$. This cyclic derivative is the chief product of the reaction; it dissolves in cold alkali hydroxide and has no basic properties. Hydrochloric acid hydrolyses it to glycine hydrochloride and hydrogen sulphide.

2 : 5-*Dithiopiperazine* turns brown at about 160°, and black at 270—280°; the *lead* and *mercury* salts are light brown; the *silver* salt separates in a gelatinous condition, and begins to decompose at once with the formation of black silver sulphide.

Thioglycylglycinethioamide is a dark brown powder, m. p. 89—95° (decomp.). E. F. A.

The Rules of Substitution in the Benzene Nucleus. Arnold H. Holleman (*Bull. Soc. chim.*, 1911, [iv], **9**, i—xlv).—A lecture delivered before the French Chemical Society. W. G.

The Study of Isomorphous Sulphonic Derivatives of Benzene. Henry A. Miers, Henry E. Armstrong, William J. Pope, and William P. Wynne (*Brit. Assoc. Reports*, 1910, 100).—This report refers to the results obtained by the examination of twenty-nine derivatives of the 1 : 4 series (Barlow and Pope, Trans., 1910, **97**, 2308), and which are found to be in accordance with Barlow and Pope's theory correlating molecular structure with crystalline form. T. S. P.

Benzylindene. Rudolf Weissgerber (*Ber.*, 1911, **44**, 2216).—Benzylindene was described in 1906 by Thiele, who showed that Marckwald's so-called benzylindene was really dibenzylindene accompanied by a little viscous oil. The author has succeeded in solidifying this oil, and shows that it is identical with his benzylindene, m. p. 33—34°. C. S.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. Frederic S. Kipping, Kennedy J. P. Orton, Siegfried Ruhemann, Arthur Lapworth, and John T. Hewitt (*Brit. Assoc. Reports*, 1910, 85—99).—This report [with William J. Jones] deals with the chlorination of anilides and the transformation of acylchloroaminobenzenes, and with the bromination of anilides and the conversion of bromoamines. T. S. P.

Two New Forms of 2-Nitro-6-hydroxylaminotoluene. Kurt Brand (*Ber.*, 1911, **44**, 2045—2047).—When crude nitrohydroxylaminotoluene prepared by electrolysis (compare Brand and Zöller, Abstr., 1907, i, 755) is dissolved in boiling benzene, it first crystallises in slender, yellow needles, changing to a stable, almost colourless form, which differs from the stable, short, yellow crystals previously

described. Three forms, two stable and one unstable, of nitrohydroxylaminotoluene therefore exist. The unstable form has not yet been separated pure from benzene. It is converted into either of the stable forms on inoculation. Further, solutions of either of the stable forms in hot benzene, inoculated with a crystal of the other form and allowed to cool slowly, yield the other form, or in some cases a mixture of the two stable forms. The stable yellow form has m. p. 117—117·5°; the colourless form becomes yellow at 105° and melts at 115° or 117—117·5°, the former figure applying to an incompletely converted sample. E. F. A.

Condensation of a Substituted Formamide to a Derivative of Aminomalonamide. HERMANN DECKER and PAUL BECKER (*Annalen*, 1911, 382, 369—377).—The formyl derivative of phenylethylamine (Bischler and Napieralski, Abstr., 1893, i, 608) reacts with phosphoric oxide or zinc chloride, yielding a product identical with that obtained by Decker and Kropp (Abstr., 1909, i, 513) by the action of phosphorus pentachloride and aluminium chloride. The product is a phosphate of the base $C_{27}H_{31}O_2N_3$, and has been obtained in a crystalline form. As the base is mono-acid and on hydrolysis loses two molecules of β-phenylethylamine and one of carbon dioxide, yielding β-phenylethylglycine, which can be synthesised from chloroacetic acid and β-phenylethylamine, the conclusion is drawn that it is β-phenylethylaminomalondiphenylethylamide. A strong odour of β-phenylethylcarbylamine is noticed during the condensation, and it is possible that the carbylamine is an intermediate product in the formation of the base.

β-Phenylethylaminomalon-β-phenylethylamide,

$$CH_2Ph\cdot CH_2\cdot NH\cdot CH(CO\cdot NH\cdot CH_2\cdot CH_2Ph)_2,$$

yields a *phosphate*, which crystallises from 95% alcohol in slender, colourless needles, m. p. 176—178°. The *picrate*, $C_{33}H_{34}O_9N_6$, separates from alcohol in well-developed crystals, m. p. 192°. The *hydrochloride*, $C_{27}H_{31}O_2N_3,HCl$, crystallises from 80% alcohol containing hydrogen chloride in colourless plates, m. p. 184—186°, and the *platinichloride*, $2C_{27}H_{31}O_2N_3,H_2PtCl_6$, crystallises from alcohol in yellowish-red, glistening plates, m. p. 254—255°. The free base, obtained by the action of ammonia on the picrate, crystallises from 80% alcohol in slender needles, m. p. 85°. Both the base and its salts have an extremely bitter taste. When the base is hydrolysed with 15% hydrochloric acid and alcohol, *β-phenylethylglycine hydrochloride*, $CH_2Ph\cdot CH_2\cdot NH\cdot CH_2\cdot CO_2H,HCl$, is formed. It crystallises from dilute acid in colourless plates, m. p. 243—244° (decomp.) when rapidly heated. *β-Phenylethylglycine*, $CH_2Ph\cdot CH_2\cdot NH\cdot CH_2\cdot CO_2H$, crystallises from 80% alcohol in slender, colourless needles, m. p. 274—276°, and dissolves readily in acids and alkalis.

Alcoholic potassium hydroxide solution also hydrolyses the base in a similar manner. J. J. S.

Doubly Linked Carbon Atoms and the Carbon–Nitrogen Linking. VIII. Reduction of *N*-Alkylated Amino-ketones. HERMANN EMDE and ERNST RUNNE (*Arch. Pharm.*, 1911, 249, 354—370. Compare this vol., i, 281).—*a-Phenylacetonyltrimethylammonium bromide*,

$COMe \cdot CHPh \cdot NMe_3Br$, an oil obtained from α-bromo-α-phenylacetone and 33% alcoholic trimethylamine in a freezing mixture, has been converted into the *aurichloride*, m. p. 158—159°, and the *platinichloride*, m. p. 207—208° (decomp.). The corresponding chloride is not attacked by zinc and dilute sulphuric acid, and is decomposed by sodium amalgam and dilute hydrochloric acid at 0°, yielding trimethylamine and phenylacetone (a portion of which is reduced to the carbinol). *α-Phenylacetonyldimethylamine hydrochloride*,

$$COMe \cdot CHPh \cdot NMe_2,HCl,$$

m. p. 193—195°, ultimately obtained from α-bromo-α-phenylacetone and dimethylamine in cold benzene, is converted into α-phenylacetone and dimethylamine by sodium amalgam in faintly acid solution. *α-Phenylacetonylmethylamine hydrochloride*,

$$COMe \cdot CHPh \cdot NHMe,HCl,$$

m. p. 210—211° (decomp.), obtained in a similar manner by means of methylamine, is only decomposed to a small extent by sodium amalgam in acid solution, the chief product being *α-methylamino-α-phenyl*iso*propyl alcohol*, $NHMe \cdot CHPh \cdot CHMe \cdot OH$, a yellow oil which forms a *hydrochloride*, m. p. 191—193°, and a *platinichloride*, m. p. 193—194° (decomp.). Betaine hydrochloride is scarcely attacked by sodium amalgam.

From these and from numerous other examples quoted from the literature, the authors state that the carbonyl group (carbon–oxygen double linking), except when present in a carboxyl group, diminishes, even to a greater extent than does the carbon double linking under otherwise the same conditions, the stability of a neighbouring single carbon–nitrogen linking during reduction. In a substance,

$$R \cdot CH_2(NH_2) \cdot COR',$$

three factors exert an influence in weakening the carbon–nitrogen linking, namely, carbon double linkings in R, the carbonyl group, and the loading of the amino-group with methyl groups; the influence of the last factor is very slight for primary and secondary amino-groups (Abstr., 1909, i, 708, 709). C. S.

Contradiction of E. Biilmann's Interpretation of Homochromoisomerism as Polymorphism. Arthur Hantzsch (*Ber.*, 1911, 44, 2001—2009).—Polemical (compare Hantzsch, Abstr., 1910, i, 474; Biilmann, this vol., i, 367). The author upholds his contention that the two phenylmethylpicramides are isomeric and not polymorphic. E. F. A.

o- and m-Iodo-p-tolyl Methyl Ether and Derivatives with Multivalent Iodine. Carl Willgerodt and Rudolph Schloss (*Ber.*, 1911, 44, 1708—1711).—A mixture of *m*- and *o*-iodo-*p*-tolyl methyl ethers is obtained by boiling a glacial acetic acid solution of *p*-tolyl methyl ether with iodine chloride until hydrogen chloride ceases to be evolved, then pouring into water, and shaking with sulphurous acid. The *o*-iodo-compound has b. p. 237—238° (compare Schall and Dralle, Abstr., 1885, 146), and the *meta*-compound, $C_6H_3IMe \cdot OMe$, crystallises from dilute alcohol in colourless, rhombic plates, m. p. 75°. *p-Tolyl methyl ether o-iododichloride*, $OMe \cdot C_6H_3Me \cdot ICl_2$, separates from light

petroleum in yellow needles, which decompose rapidly on exposure to the air, regenerating the original iodo-compound.

Phenyl-p-*methoxy*-o-*tolyliodonium iodide*, $OMe \cdot C_6H_3Me \cdot IPhI$, obtained from the iodo-dichloride and mercury diphenyl in the presence of a few drops of water, and subsequent treatment with potassium iodide, crystallises from alcohol in pale yellow needles, m. p. 181°.

p-*Tolyl methyl ether* m-*iododichloride*, $OMe \cdot C_6H_3Me \cdot ICl_2$, forms orange-yellow, felted needles, decomposing at 58—60°. The corresponding *iodoso*-compound, $OMe \cdot C_6H_3Me \cdot IO$, forms a pale yellow, amorphous powder, which decomposes at 176°. It does not yield the corresponding iodoxy-compound when warmed with water or treated with sodium hypochlorite solution. The *iodosoacetate*,

$$OMe \cdot C_6H_3Me \cdot I(OAc)_2,$$

forms long, glistening crystals, m. p. 120—122°, and *phenyl*-p-*methoxy*-m-*tolyliodonium iodide*, $C_{14}H_{14}OI_2$, crystallises from alcohol, and has m. p. 166°. J. J. S.

Products of the Action of Nitric Acid on Dihydroanethole. HERMANN THOMS and W. DRAUZBURG (*Ber.*, 1911, **44**, 2125—2133).—When heated with 45% nitric acid, dihydroanethole (*p*-methoxypropylbenzene) yielded the following products: (1) Anisic acid. (2) Anisaldehyde. (3) 3-*Nitro*-4-*methoxypropylbenzene*, $OMe \cdot C_6H_3Pr^{\alpha} \cdot NO_2$, which is an almost colourless liquid, b. p. 164—169°/9 mm., solidifying at −6°; it is oxidised by potassium permanganate and dilute sulphuric acid to 3-nitroanisic acid. (4) 2:6-*Dinitro*-4-*propylphenol*,

$$OH \cdot C_6H_2Pr^{\alpha}(NO_2)_2,$$

which crystallises from ether in yellow, prismatic columns, m. p. 46°; the *sodium* salt forms dark reddish-green needles, which sinter at 264° and decompose explosively; the *potassium* and *silver* salts are also mentioned. The *acetyl* derivative crystallises in greenish-yellow needles, m. p. 89°; the *benzoyl* derivative has m. p. 86·5—87°. When heated with diphenylcarbamyl chloride and pyridine, the dinitrophenol yields a *diphenylurethane*, $NPh_2 \cdot CO \cdot O \cdot C_6H_2Pr^{\alpha}(NO_2)_2$, crystallising in cubes, m. p. 136·5°.

4-*Methylcarbonato*-3:5-*dinitro*-1-*propylbenzene*,

$$CO_2Me \cdot O \cdot C_6H_2Pr^{\alpha}(NO_2)_2,$$

prepared by the action of methyl chlorocarbonate on the sodium salt, crystallises in almost white needles, m. p. 85·5—86·5°.

The dinitrophenol is reduced by tin and hydrochloric acid to 2:6-*diamino*-4-*propylphenol*, which is unstable in the free condition, and is, therefore, best isolated in the form of the *hydrochloride*, $OH \cdot C_6H_2Pr^{\alpha}(NH_2)_2,2HCl$; the *benzoyl* derivative forms rosettes of slender needles, m. p. 198°. 2:6-*Diacetylamino*-4-*propylphenol*, $OH \cdot C_6H_2Pr^{\alpha}(NHAc)_2$, prepared by the gradual addition of acetic anhydride to a solution of the diamine hydrochloride in the presence of a slight excess of sodium acetate and acetic acid, crystallises in needles, m. p. 161·5—162°. The action of nitrous acid on the diaminophenol results in the formation of a brown *dye*.

Since 2:6-dinitro-4-propylphenol is also obtained by nitrating 3-nitro-4-methoxypropylbenzene, it is probable that the latter compound

is formed as an intermediate product in the preparation of the dinitrophenol from dihydroanethole by the action of nitric acid.

The above-mentioned transformations of dihydroanethole and its nitro-derivative into dinitropropylphenol constitute the first recorded examples of the oxidation of the methoxy-group to hydroxyl by means of nitric acid. F. B.

The Elimination of Methoxy-groups from Phenolic Ethers by means of Nascent Hydrogen. HERMANN THOMS and W. SIEBELING (*Ber.*, 1911, 44, 2134—2136).—The action of sodium on pyrogallol trimethyl ether in alcoholic solution leads to the formation of resorcinol dimethyl ether, the methoxy-group in position 2 being readily replaced by hydrogen. *iso*Eugenyl methyl ether, when subjected to the same treatment, yields a small quantity of a phenol, whilst in the case of anethole, *m*-methoxypropylbenzene, and asarone no replacement of the methoxy-group was observed.

From these results the authors draw the conclusion that the ready elimination of a methoxy-group from pyrogallol trimethyl ether is due to the accumulation of methoxy-groups in adjacent positions, and not to the presence of a substituent in the para-position (compare Semmler, Abstr., 1908, i, 557, 734; Kostanecki and Lampe, *ibid.*, 442). F. B.

Stereoisomeric β-Nitro-α-methoxy-αβ-diphenylethanes prepared by the Addition of Alkali Methoxide to 7-Nitrostilbene. FRIEDRICH HEIM (*Ber.*, 1911, 44, 2013—2016. Compare Meisenheimer and Heim, Abstr., 1907, i, 858).—By the interaction of 7-nitrostilbene and sodium methoxide, two stereoisomeric β-nitro-α-methoxy-αβ-diphenylethanes, $OMe\cdot CHPh\cdot CHPh\cdot NO_2$, are formed, distinguished as α, m. p. 130—131°, and β, m. p. 97—98°, modifications (Meisenheimer and Heim, *loc. cit.*). It is now shown that both modifications are formed simultaneously, and that by varying the conditions, one or other is obtained in larger quantity, although the less fusible form always preponderates. The isomerides are separated by crystallisation from light petroleum and mechanical sorting, the α-form yielding slender, colourless needles, and the β-isomeride stumpy, transparent crystals. The isomerides are precipitated from the reaction mixture either by means of carbon dioxide, which favours the formation of the β-isomeride, or by ammonium chloride and air, a process most favourable to the α-modification.

On heating above the melting point, the β-isomeride is the more stable, being nearly all recovered after heating at 170°. The α-isomeride at this temperature becomes dark brown, and liberates fumes with the odour of a nitrile. In neither instance did heating bring about conversion into the other isomeride. E. F. A.

Condensation of ω-Nitrotoluene with Benzaldehyde. *cis*- and *trans*-7-Nitrostilbene. FRIEDRICH HEIM (*Ber.*, 1911, 44, 2016—2022).—On condensing benzaldehyde with ω-nitrotoluene, in addition to the 7-nitrostilbene obtained by Knoevenagel and Walter (Abstr., 1905, i, 65), m. p. 75°, a second isomeride is formed.

ponents. 2-Ethoxy-α-naphthaldehyde condenses with malonic acid in alcoholic solution in the presence of aniline, yielding β-naphthacoumarin-3-carboxylic acid (compare Bartsch, *loc. cit.*; Knoevenagel and Schröter, Abstr., 1905, i, 63). Attempts to condense the aldehyde with ethyl acetate and ethyl malonate proved unsuccessful.

ω-ω-2-*Trichloro*-1-*methylnaphthalene*, $C_{10}H_6Cl\cdot CHCl_2$, obtained by heating 2-hydroxy-1-naphthaldehyde with phosphorus pentachloride at 193—205°, crystallises from alcohol in rhombic plates, m. p. 90°; when heated with methyl-alcoholic sodium methoxide it yields 2-*chlorodi*-ω-*methoxy*-1-*methylnaphthalene*, $C_{10}H_6Cl\cdot CH(OMe)_2$, which crystallises in white prisms capped with small pyramids, m. p. 86°.

2-*Chloro*-1-*naphthaldehyde*, $C_{10}H_6Cl\cdot CHO$, prepared by heating the preceding trichloro-compound with dilute acetic acid, or with sodium acetate in aqueous alcoholic solution, crystallises in long, flexible, white needles, m. p. 76°, and gives with strong sulphuric acid a yellow coloration, which becomes blood-red on the addition of nitric acid; the *azine*, $C_{22}H_{14}N_2Cl_2$, forms stout, golden-yellow needles, m. p. 195°, the *semicarbazone*, $C_{12}H_{10}ON_3Cl$, slender, microscopic needles, m. p. 215°. When heated with anhydrous potassium acetate and acetic anhydride at 170°, it yields β-2-*chloro*-1-*naphthylacrylic acid*, $C_{10}H_6Cl\cdot CH{:}CH\cdot CO_2H$, which crystallises in long needles, m. p. 176°, and furnishes a crystalline *ammonium* and an amorphous *calcium* salt; the salts of the *alkali metals* and of *silver* are also mentioned. On account of its instability, the *chloride* could not be isolated. The *amide*, $C_{10}H_6Cl\cdot CH{:}CH\cdot CO\cdot NH_2$, crystallises in stout, white needles, m. p. 195°. The acid is reduced by sodium amalgam, chlorine being eliminated from the nucleus at the same time. All attempts to effect an internal condensation in the peri-position by means of sulphuric acid, zinc chloride, or phosphoric oxide were unsuccessful.

Di-2-*chloro*-1-*naphthylideneacetone*, $CO(CH{:}CH\cdot C_{10}H_6Cl)_2$, is obtained by condensing 2-chloro-1-naphthaldehyde with acetone by means of strong sulphuric acid. It crystallises from ethyl benzoate in canary-yellow needles, m. p. 215°, and gives with concentrated sulphuric acid an indigo-blue coloration.

α-2-*Chloro*-1-*naphthyl*-Δ^{α}-*penten*-γ-*one*, $C_{10}H_6Cl\cdot CH{:}CH\cdot COEt$, prepared by the condensation of 2-chloro-1-naphthaldehyde and methyl ethyl ketone by means of potassium hydroxide in aqueous alcoholic solution, crystallises in flexible, white needles, m. p. 74°, and gives with strong sulphuric acid a reddish-brown coloration, which almost disappears on the addition of nitric acid; the *semicarbazone*,

$$C_{16}H_{16}ON_3Cl,$$

forms lustrous, silky needles, m. p. 185°. When the condensation is carried out in very feebly alkaline solution, α-2-*chloro*-1-*naphthylpentan*-γ-*one*-α-*ol*, $C_{10}H_6Cl\cdot CH(OH)\cdot CH_2\cdot COEt$, is produced. This crystallises in large double pyramids, m. p. 124°, and is converted by the action of aqueous alcoholic potassium hydroxide into the above-mentioned unsaturated ketone.

α-2-*Chloro*-1-*naphthylpentan*-γ-*one*, $C_{10}H_6Cl\cdot CH_2\cdot CH_2\cdot COEt$, is obtained in the form of a viscid oil by reducing the unsaturated chloroketone with aluminium amalgam in ethereal solution. Attempts to

effect an internal condensation in the peri-position by the action of dehydrating agents yielded no definite results. When treated with semicarbazide, it yields a *substance*, $C_{16}H_{15}ON_2Cl$, the constitution of which has not yet been determined. F. B.

Labile Isomerides of the Same Structure, which can be Converted One into Another. EMIL ERLENMEYER (*Biochem. Zeitsch.*, 1911, 34, 306—353).—The author gives the history of the discovery of the various isomerides of cinnamic acid discovered by Liebermann and Erlenmeyer, sen., and of the additions made to the knowledge of these acids by himself and his pupils. He considers that the following labile acids, of which the crystals have been measured, are known to exist, namely: *iso*Cinnamic acid of Erlenmeyer, sen., the *iso*cinnamic acid in dextrohemihedral and holohedral forms of Liebermann, hemihedral and holohedral forms of *allo*cinnamic acid, and triclinic cinnamic acid. There are, therefore, more isomerides than can be accounted for from the structure and chemical configuration, and the author explains the differences on the assumption of a difference of space disposition in some part of the molecule, the exact character of which is not yet known. He draws the following conclusions from the investigations summarised in this communication. The *iso*-acid as originally described by Erlenmeyer, sen., exists, and possesses the properties originally ascribed to it. It can be changed, however, into the *allo*-acid; it gives with aniline, as Liebermann showed, the aniline salt of the *allo*-acid. The latter acid on treatment with small quantities of an alcoholic solution of zinc bromide is converted into the Erlenmeyer *iso*-acid. The *iso*-acid (E) is also converted into the *allo*-form when left in contact with dilute sulphuric acid. The *iso*-acid of Liebermann prepared from natural sources also exists, and has m. p. 58—59° (from light petroleum); it spontaneously changes into the *allo*-acid, and can be prepared by the reduction of the α-bromo*allo*cinnamic acid. It is an actual modification and not merely a component of the *iso*-acid (L). In addition to existence in nature, it can also be prepared artificially: (*a*) by making the brucine salt of the *allo*-acid, and (*b*) by reduction of the α-bromo*allo*-acid. When the *allo*-acid is neutralised with brucine, two salts can be separated from one another by fractional crystallisation, which differ from one another in solubility, melting point, polarisation, etc. One of these yields the *iso*-acid (L) in hemihedral, and the other the *iso*-acid of holohedral, form. Possibly three brucine salts are formed when the acid is neutralised in this way.

S. B. S.

Constitution of Dehydracetic Acid. WILLIAM J. HALE (*J. Amer. Chem. Soc.*, 1911, 33, 1119—1135).—Evidence of a positive and of a negative character is advanced to support Feist's rather than Collie's formula of dehydracetic acid. The negative evidence is based on the fact that sodionitromalonic aldehyde, which reacts very readily with the group $\cdot CH_2\cdot CO\cdot CH_2\cdot$, does not attack dehydracetic acid. The positive evidence is of two kinds. Firstly, Goldschmiedt, Harries, and others have shown that aromatic aldehydes react with saturated asymmetrical ketones in two ways, preferably with the methyl group

ponents. 2-Ethoxy-α-naphthaldehyde condenses with malonic acid in alcoholic solution in the presence of aniline, yielding β-naphthacoumarin-3-carboxylic acid (compare Bartsch, *loc. cit.*; Knoevenagel and Schröter, Abstr., 1905, i, 63). Attempts to condense the aldehyde with ethyl acetate and ethyl malonate proved unsuccessful.

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α-2-*Chloro*-1-*naphthylpentan*-γ-*one*, $C_{10}H_6Cl\cdot CH_2\cdot CH_2\cdot COEt$, is obtained in the form of a viscid oil by reducing the unsaturated chloroketone with aluminium amalgam in ethereal solution. Attempts to

effect an internal condensation in the peri-position by the action of dehydrating agents yielded no definite results. When treated with semicarbazide, it yields a *substance*, $C_{16}H_{15}ON_2Cl$, the constitution of which has not yet been determined. F. B.

Labile Isomerides of the Same Structure, which can be Converted One into Another. EMIL ERLENMEYER (*Biochem. Zeitsch.*, 1911, 34, 306—353).—The author gives the history of the discovery of the various isomerides of cinnamic acid discovered by Liebermann and Erlenmeyer, sen., and of the additions made to the knowledge of these acids by himself and his pupils. He considers that the following labile acids, of which the crystals have been measured, are known to exist, namely: *iso*Cinnamic acid of Erlenmeyer, sen., the *iso*cinnamic acid in dextrohemihedral and holohedral forms of Liebermann, hemihedral and holohedral forms of *allo*cinnamic acid, and triclinic cinnamic acid. There are, therefore, more isomerides than can be accounted for from the structure and chemical configuration, and the author explains the differences on the assumption of a difference of space disposition in some part of the molecule, the exact character of which is not yet known. He draws the following conclusions from the investigations summarised in this communication. The *iso*-acid as originally described by Erlenmeyer, sen., exists, and possesses the properties originally ascribed to it. It can be changed, however, into the *allo*-acid; it gives with aniline, as Liebermann showed, the aniline salt of the *allo*-acid. The latter acid on treatment with small quantities of an alcoholic solution of zinc bromide is converted into the Erlenmeyer *iso*-acid. The *iso*-acid (E) is also converted into the *allo*-form when left in contact with dilute sulphuric acid. The *iso*-acid of Liebermann prepared from natural sources also exists, and has m. p. 58—59° (from light petroleum); it spontaneously changes into the *allo*-acid, and can be prepared by the reduction of the α-bromo*allo*cinnamic acid. It is an actual modification and not merely a component of the *iso*-acid (L). In addition to existence in nature, it can also be prepared artificially: (*a*) by making the brucine salt of the *allo*-acid, and (*b*) by reduction of the α-bromo*allo*-acid. When the *allo*-acid is neutralised with brucine, two salts can be separated from one another by fractional crystallisation, which differ from one another in solubility, melting point, polarisation, etc. One of these yields the *iso*-acid (L) in hemihedral, and the other the *iso*-acid of holohedral, form. Possibly three brucine salts are formed when the acid is neutralised in this way.

S. B. S.

Constitution of Dehydracetic Acid. WILLIAM J. HALE (*J. Amer. Chem. Soc.*, 1911, 33, 1119—1135).—Evidence of a positive and of a negative character is advanced to support Feist's rather than Collie's formula of dehydracetic acid. The negative evidence is based on the fact that sodionitromalonic aldehyde, which reacts very readily with the group $\cdot CH_2\cdot CO\cdot CH_2\cdot$, does not attack dehydracetic acid. The positive evidence is of two kinds. Firstly, Goldschmiedt, Harries, and others have shown that aromatic aldehydes react with saturated asymmetrical ketones in two ways, preferably with the methyl group

adjacent to the carbonyl group in alkaline solution, but with the methylene group in the presence of acid. Dehydracetic acid (and also dehydracetocarboxylic acid), constituted in accordance with Feist's views, allows of the formation of one benzylidene derivative by condensation with benzaldehyde. Collie's formulation of the two acids permits of the possibility of three ways of condensation, and the probability of the formation of two benzylidene compounds in acid solution. The facts are, however, that dehydracetic acid and dehydracetocarboxylic acid do not condense with benzaldehyde in acid solution, whilst in aqueous sodium hydroxide, one benzylidene compound of each is obtained; *benzylidenedehydracetocarboxylic acid*, $CHPh{:}CH{\cdot}CO{\cdot}CH{<}{\genfrac{}{}{0pt}{}{CO\text{———}O}{CO{\cdot}C(CO_2H)}}{>}CMe$, has m. p. 147—148° (corr.), and *benzylidenedehydracetic acid*, $CHPh{:}CH{\cdot}CO{\cdot}CH{<}{\genfrac{}{}{0pt}{}{CO\text{—}O}{CO{\cdot}CH}}{>}CMe$, has m. p. 105—106° (corr.), both compounds yielding dehydracetic acid by sublimation.

Further evidence against Collie's formula for dehydracetic acid is obtained by an examination of von Pechmann's synthesis of the acid from acetonedicarboxylic acid and acetic anhydride or acetyl chloride. Both Feist and Collie indicate possible courses of this reaction which lead each to his own constitution of dehydracetic acid. The author shows that acetonedicarboxylic acid, when heated on the water-bath with an excess of benzoic anhydride or benzoyl chloride, yields s-*dibenzoylacetonedicarboxylic acid*, $CO_2H{\cdot}CHBz{\cdot}CO{\cdot}CHBz{\cdot}CO_2H$, m. p. 162° (corr.), which reacts with acetic anhydride and a few drops of concentrated sulphuric acid, yielding dehydracetocarboxylic and benzoic acids, owing to a displacement of the benzoyl by acetyl groups. There is little doubt, therefore, that the initial step in von Pechmann's reaction is the direct interaction of the methylene hydrogen atoms of acetonedicarboxylic acid with the acetic anhydride; Collie's explanation would not permit of a reaction between acetonedicarboxylic acid and benzoic anhydride.

s-Dibenzoylacetonedicarboxylic acid contains four ionisable hydrogen atoms, decomposes when heated, and is easily hydrolysed to benzoic and acetonedicarboxylic acids. Its *diethyl* ester, $C_{23}H_{22}O_7$, m. p. 70·5° (corr.), contains two ionisable hydrogen atoms, also decomposes when heated, and does not react with acetic anhydride; it is hydrolysed by boiling aqueous barium hydroxide, yielding benzoic and acetonedicarboxylic acids. C. S.

Conversion of Substituted Paraconic Acids into the Isomeric *cyclo*Propanedicarboxylic Acids. PHILIPPE BARBIER and RÉNÉ LOCQUIN (*Compt. rend.*, 1911, 153, 188—191).—Phenylparaconic acid and terebic acid, when their solutions in about one and a-half times the weight of benzene are heated for twelve hours with thionyl chloride on the water-bath, are converted into the anhydrides of *cis*-3-phenyl*cyclo*propane-1 : 2-dicarboxylic acid and *cis*-3 : 3-dimethyl*cyclo*propane-1 : 2-dicarboxylic acid respectively, sulphur dioxide and

hydrogen chloride being evolved. The reaction, which appears to be a general one for lactonic acids, follows probably the course:

$$CO_2H\cdot CH<\begin{matrix}CHPh\cdot O\\ CH_2-CO\end{matrix} \xrightarrow{SOCl_2} CO_2H\cdot CH<\begin{matrix}CHPh\cdot O\cdot SOCl\\ CH_2\cdot COCl\end{matrix} \rightarrow$$

$$SO_2+HCl+CO_2H\cdot CH<\begin{matrix}CHPh\\ CH\cdot COCl\end{matrix} \rightarrow HCl+CHPh<\begin{matrix}CH\cdot CO\\ CH\cdot CO\end{matrix}>O.$$

C. S.

Spectrographic Studies in the Phthalein Group. RICHARD MEYER and OTTO FISCHER (*Ber.*, 1911, **44**, 1944—1954).—With the object of ascertaining the cause of the difference in colour exhibited by the *p*-hydroxy- and di-*p*-hydroxy-derivatives of triphenylmethane, the authors have examined the ultra-violet absorption spectra of the sodium salts of phenolphthalein, tetrabromophenolphthalein, fluorescein, quinolphthalein, *p*-hydroxyphenylphthalide, and *p*-hydroxydiphenylphthalide in aqueous solution.

It is found that the spectra of the four first-named compounds are all similar in character, and show well-marked absorption bands, which, however, are lacking in the case of the salts of *p*-hydroxyphenylphthalide and *p*-hydroxydiphenylphthalide, but whether these results support the view put forward by Baeyer (Abstr., 1907, i, 754) that the colour of the disubstituted derivatives of triphenylmethane is due to a rhythmic movement in the molecule, whereby each of the two substituted benzene nuclei alternately acquire a quinonoid structure, has not been determined.

The following new derivatives of *p*-hydroxyphenylphthalide and *p*-hydroxydiphenylphthalide are described.

p-*Benzoyloxyphenylphthalide*, $CO<\begin{matrix}C_6H_4\\ O\end{matrix}>CH\cdot C_6H_4\cdot OBz$, crystallises in colourless, rectangular plates, m. p. 188°. p-*Ethoxyphenylphthalide*, $C_{16}H_{14}O_3$, prepared by the action of ethyl iodide and alcoholic sodium ethoxide on *p*-hydroxyphenylphthalide, forms rhombic plates, m. p. 116°; the corresponding *benzyl ether*, $C_{21}H_{16}O_3$, crystallises in prismatic needles, m. p. 180°. The *anilide*,

$$CO<\begin{matrix}C_6H_4\\ NPh\end{matrix}>CH\cdot C_6H_4\cdot OH,$$

prepared by heating *p*-hydroxyphenylphthalide with aniline and aniline hydrochloride, forms colourless needles, which become brown at 250° and have m. p. 267°.

p-*Benzoyloxydiphenylphthalide*, $CO<\begin{matrix}C_6H_4\\ O\end{matrix}>CPh\cdot C_6H_4\cdot OBz$, crystallises in triangular prisms, m. p. 139°.

p-*Ethoxydiphenylphthalide*, $C_{22}H_{18}O_3$, forms quadratic plates, m. p. 88°; the *methoxy*-derivative, $C_{21}H_{16}O_3$, prepared by methylating *p*-hydroxydiphenylphthalide with methyl sulphate and potassium hydroxide, crystallises in rectangular prisms, m. p. 86°; the *benzyl ether*, $C_{27}H_{20}O_3$, crystallises from glacial acetic acid in rectangular prisms, m. p. 109°.

The *anilide*, $CO<\substack{C_6H_4 \\ NPh}>CPh\cdot C_6H_4\cdot OH$, forms hexagonal plates, m. p. 276°. F. B.

Action of Nitric Acid on Trimethylgallic [3 : 4 : 5-Trimethoxybenzoic] Acid and its Methyl Ester. Constitution of Antiarol. HERMANN THOMS and W. SIEBELING (*Ber.*, 1911, **44**, 2115—2125).—When 3 : 4 : 5-trimethoxybenzoic acid in glacial acetic acid solution is treated with fuming nitric acid at −15°, the carboxyl group is displaced by a nitro-group, with the formation of 5-nitropyrogallol trimethyl ether (compare Schiffer, Abstr., 1892, i, 715).

Nitration under similar conditions, but at a higher temperature, results in the formation of 5 : 6-dinitropyrogallol trimethyl ether, which has m. p. 119°, and not 126°, as given by Will (Abstr., 1888, 457).

The nitration of methyl 3 : 4 : 5-trimethoxybenzoate yields either methyl 2-nitro-3 : 4 : 5-trimethoxybenzoate or *methyl* 2 : 6-*dinitro*-3 : 4 : 5-*trimethoxybenzoate*, according to the conditions under which the reaction is carried out. The last-named compound, which crystallises in colourless needles, m. p. 111°, is obtained by the gradual addition of fuming nitric acid to a glacial acetic acid solution of the ester, the reaction being completed by warming the mixture.

2-*Nitro*-3 : 4 : 5-*trimethoxybenzoic acid*, prepared by hydrolysing the corresponding methyl ester with alcoholic potassium hydroxide, crystallises from benzene in colourless prisms, m. p. 163—164°, which lose carbon dioxide when heated at 190—220°; the *silver* and *barium* salts were analysed. When warmed with strong nitric acid the carboxyl group is displaced by the nitro-group with the formation of 5 : 6-dinitropyrogallol trimethyl ether.

2 : 6-*Dinitro*-3 : 4 : 5-*trimethoxybenzoic acid*, $C_6(OMe)_3(NO_2)_2\cdot CO_2H$, obtained by the hydrolysis of the methyl ester with dilute alcoholic potassium hydroxide at the ordinary temperature, forms colourless needles, m. p. 158—160°, which become yellow on exposure to light; the *barium* salt crystallises in pale yellow prisms, the *silver* salt in yellow, microscopic needles. When heated at 194°, it loses carbon dioxide, yielding 4 : 6-*dinitropyrogallol trimethyl ether*,

$$C_6H(NO_2)_2(OMe)_3,$$

which forms large, yellow, transparent crystals, m. p. 85°. On further nitration by means of a mixture of fuming nitric and concentrated sulphuric acids below 20°, it is converted into 4 : 5 : 6-*trinitropyrogallol trimethyl ether*; this crystallises in slender, yellow needles, m. p. 128°.

Reduction of 6-nitropyrogallol trimethyl ether, followed by the displacement of the amino-group by hydroxyl by means of the diazo-reaction, gives rise to 5-hydroxypyrogallol trimethyl ether, m. p. 146°. The latter compound is identical with the phenol first obtained by Will (*loc. cit.*) by the partial methylation of dimethoxyquinol, and subsequently isolated by Kiliani (Abstr., 1897, i, 91) from the sap of *Antiaris toxicata*, under the name of antiarol. F. B.

Synthesis of Methyl Digallatepentamethyl Ether. FERDINAND MAUTHNER (*J. pr. Chem.*, 1911, [ii], 84, 140—143).—The 3 : 4 : 5 : 2′ : 6′-*pentamethyl ether* of *methyl digallate*,

$$C_6H_2(OMe)_3{\cdot}CO{\cdot}O{\cdot}C_6H_3(OMe)_2{\cdot}CO_2Me,$$

is formed by shaking an ethereal solution of gallyl chloride trimethyl ether (Perkin and Weizmann, Trans., 1906, 89, 1655) with an aqueous solution of the sodium derivative of methyl syringate (Graebe and Martz, Abstr., 1905, i, 703), and crystallises from a mixture of benzene and light petroleum in needles, m. p. 169—170°. When boiled for ten hours with aqueous alcoholic potassium hydroxide, it yields the trimethyl ether of gallic acid and syringic acid, which can be separated by means of their calcium salts. J. J. S.

Formation of Benzaldehyde and 2 : 4 : 6-Tribromoaniline from 3 : 5-Dibromo-4-aminobenzhydrol by the Action of Bromine. LATHAM CLARKE and GUSTAVUS J. ESSELEN, jun. (*J. Amer. Chem. Soc.*, 1911, 33, 1135—1140).—*p*-Aminobenzophenone is conveniently obtained by heating benzoyl chloride (2 mols.) and aniline for fifteen minutes at 170—180°, then adding zinc chloride, and heating again for ten hours at 200—210° (compare Chattaway, Trans., 1904, 85, 394); the resulting *p*-benzoylaminobenzophenone is hydrolysed by alcoholic sodium hydroxide.

By treatment with bromine (2 mols.) in dry chloroform, *p*-aminobenzophenone yields 3 : 5-*dibromo*-4-*aminobenzophenone*, m. p. 146°, which is reduced by aluminium amalgam to 3 : 5-*dibromo*-4-*aminobenzhydrol*, m. p. 147·5°. This substance, by bromination (1 mol.) in dry chloroform, is decomposed into benzaldehyde, hydrogen bromide, and 2 : 4 : 6-tribromoaniline. The formation of the last compound is the proof of the position of the halogen atoms in 3 : 5-dibromo-4-aminobenzophenone. C. S.

Steric Hindrance. PAVEL IW. PETRENKO-KRITSCHENKO (*J. pr. Chem.*, 1911, [ii], 84, 143—144. Compare Abstr., 1910, i, 177).—It is pointed out that Stewart (this vol., i, 210) admits that steric hindrance affords a simple explanation of the phenomena met with in the study of cyclic ketones and amines. J. J. S.

The Study of Hydro-aromatic Substances. EDWARD DIVERS, ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Brit. Assoc. Reports*, 1910, 82—84).—This report deals with the action of ethyl cyanoacetate on 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one (Trans., 1910, 97, 518) with 3 : 5-dichloro-*o*-xylene and 3 : 5-dichlorophthalic acid (Trans., 1910, 97, 98), and also with the preparation of 1 : 1 : 2-trimethyl*cyclo*hexan-3-one from trimethyldihydroresorcin. T. S. P.

New Method of Synthesis of Methyl Ketones. PHILIPPE BARBIER and RÉNÉ LOCQUIN (*Bull. Soc. chim.*, 1911, [iv], 9, 722—726). —In a previous paper (this vol., i, 708), mention was made of a new method of preparing methyl ketones. This has now been worked out as a general method, and it has been applied in particular to the

preparation of benzyl methyl ketone from methyl dimethylacetoacetate and magnesium benzyl chloride. A 40% yield resulted. In general, organo-magnesium compounds of the type R·Mg·X, by condensation with an ester of the type $\frac{R_1}{R_2}{>}C{<}\frac{CO\cdot CH_3}{CO_2R_3}$ and subsequent saponification, will yield the ketone $R\cdot CO\cdot CH_3$. Condensation with an ester of the type $CHR_1{:}C{<}\frac{CO\cdot CH_3}{CO_2X}$ yields a branched ketone of the type $CH_3\cdot CO\cdot CH_2\cdot CH{<}\frac{R}{R_1}$.

W. G.

Ketones of the Type of α-Benzyl-αα-dimethylacetophenone. Trialkylacetic Acids and Trialkylmethylcarbinols to which They Give Rise. ALBIN HALLER and ÉDOUARD BAUER (*Compt. rend.*, 1911, **153**, 21—27. Compare Abstr., 1909, i, 654).—The general method already described has been applied to the synthesis of new ketones from phenyl *iso*propyl ketone. The sodium derivative of this substance treated with *o*-xylyl bromide gives *α-o-xylyl-αα-dimethylacetophenone*, $COPh\cdot CMe_2\cdot CH_2\cdot C_6H_4Me$, b. p. 199—200°/15 mm.; the m-*xylyl* derivative is an oil, b. p. 196—197°/12 mm., whilst the p-*xylyl* derivative has b. p. 200—202°/13 mm. α-p-*Methoxybenzyl-αα-dimethylacetophenone*, $COPh\cdot CMe_2\cdot CH_2\cdot C_6H_4\cdot OMe$, is a viscid liquid, b. p. 222—224°/15 mm.

The new ketones react normally with sodamide, giving rise to the following amides. o-*Tolyl-α-methyl*iso*butyramide*, pearly spangles, m. p. 62—63°, b. p. 188—192° in a vacuum; o-*tolyl-α-methyl*iso*butyric acid*, $C_7H_7\cdot CH_2\cdot CMe_2\cdot CO_2H$, has m. p. 48°, b. p. 180—181°/16 mm. m-*Tolyl-α-methyl*iso*butyramide* has m. p. 46—47°, and the p-*tolyl* derivative, m. p. 85—86°; the two corresponding *acids* have b. p. 178°/16 mm. and m. p. 53—54°, b. p. 180°/16 mm. respectively. p-*Anisyl-α-methyl*iso*butyramide* separates from ether in prisms probably containing ether of crystallisation, m. p. 72°, after resolidification m. p. 99—100°; the *acid* has m. p. 52—53°.

On reduction with sodium and alcohol, *o*-tolyl-α-methyl*iso*butyramide gives an 80% yield of the *carbinol*, $C_7H_7\cdot CH_2\cdot CMe_2\cdot CH_2\cdot OH$, b. p. 142—143°/15 mm., and a 5—7% yield of o-*xylyldimethylethylamine*, $C_7H_7\cdot CH_2\cdot CMe_2\cdot CH_2\cdot NH_2$, b. p. 129—130°/13 mm.; the *platinichloride* is crystalline. The corresponding m-*xylyl-carbinol* has b. p. 139—140°/16 mm., and the *amine*, b. p. 134—135°/15 mm. The p-*xylyl-carbinol* has m. p. 37°, b. p. 141°/15 mm. p-*Anisyl-β-methyl*iso*butyl alcohol*, $C_7H_7O\cdot CH_2\cdot CMe_2\cdot CH_2\cdot OH$, has m. p. 50°.

W. O. W.

Synthesis of Substituted β-Diketones, Ketonic Esters, and Enolic Esters by means of Ketones and Sodamide. ALBIN HALLER and EDMOND BAUER (*Compt. rend.*, 1911, **153**, 145—152).—The sodium derivative of a ketone, $R\cdot CO\cdot CHR'_2$, reacts with acid chlorides as though $R\cdot CO\cdot CNaR'_2$ and $R\cdot C(ONa){:}CR'_2$ were both present, but with ethyl β-iodopropionate as though only the former is present. Thus phenyl *iso*propyl ketone, sodamide, and benzoyl chloride yield *ββ-dibenzoylpropane*, CBz_2Me_2, b. p. 195—196°/

15 mm., m. p. 99—100° (*oxime*, $NOH\colon CPh\cdot CBzMe_2$, m. p. 166°), and *α-phenyl-ββ-dimethylvinyl benzoate*, $CMe_2\colon CPh\cdot O\cdot COPh$, b. p. 194—196°/13·5 mm., m. p. 53—54°; the latter does not form an oxime, and is hydrolysed by cold alcoholic potassium hydroxide or 1% methyl-alcoholic hydrogen chloride, whilst the former is converted into benzoic acid and phenyl *iso*propyl ketone by boiling alcoholic potassium hydroxide. Similarly, *iso*propyl *tert.*-butyl ketone, sodamide, and benzoyl chloride in benzene yield *β-benzoyl-β-pivaloylpropane*, $CMe_3\cdot CO\cdot CMe_2\cdot COPh$, m. p. 35° (*oxime*, m. p. 178°), and an oil which is shown to contain the *benzoate*, $CMe_2\colon C(OBz)\cdot CMe_3$. Pivaloyl chloride, *iso*propyl *tert.*-butyl ketone, and sodamide in benzene yield a liquid, b. p. 213—214° or 102°/18 mm., which doubtless is a mixture of ββ-dipivaloylpropane and the isomeric enolic ester; it does not form an oxime or semicarbazone.

Ethyl β-iodopropionate, phenyl *iso*propyl ketone, and sodamide in ether yield mainly *ethyl γ-benzoyl-γ-methylvalerate*,

$$CBzMe_2\cdot CH_2\cdot CH_2\cdot CO_2Et,$$

b. p. 183°/13 mm. (*oxime*, m. p. 119—120°), which is hydrolysed by potassium hydroxide to the *acid*, an oil which forms an *oxime*, $NOH\colon CPh\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CO_2H$, m. p. 123—124°. Under similar conditions ethyl β-iodopropionate and phenyl propyl ketone yield *ethyl γ-benzoylhexoate*, $CO_2Et\cdot CH_2\cdot CH_2\cdot CHEtBz$, b. p. 189—191°/15 mm. (p-*nitrophenylhydrazone*, yellow crystals, m. p. 205°).

Summarising this and Claisen's work, it is seen that with the sodium derivatives of ketones: (1) acid chlorides and ethyl chloroformate yield isomeric C and O derivatives; (2) ethyl chloro- or bromo-acetate yields glycide esters; (3) ethyl β-iodopropionate, like the alkyl halides, reacts normally and yields δ-ketonic esters. C. S.

Explanation of the Reaction between *p*-Benzoquinone and Hydrogen Chloride. JULIUS SCHMIDLIN (*Ber.*, 1911, 44, 1700—1705. Compare Posner, Abstr., 1904, i, 1029; 1909, i, 809; Michael, Abstr., 1904, ii, 164; 1909, i, 494; 1910, i, 748).—The author draws attention to the equilibrium which exists between *p*-benzoquinone and chloroquinol on the one hand, and chloro-*p*-benzoquinone and quinol on the other: $O\colon C_6H_4\colon O + C_6H_3Cl(OH)_2 \rightleftarrows O\colon C_6H_3Cl\colon O + C_6H_4(OH)_2$.

In the reaction between hydrogen chloride and quinone the conclusion is drawn that the quinone combines with hydrogen chloride, and that the resulting chloroquinol reacts with the quinone, yielding chloro-*p*-benzoquinone and quinol. The equilibrium is disturbed by the separation of quinol in the form of the sparingly soluble quinhydrone, and thus all the free *p*-benzoquinone is transformed into chloro-*p*-benzoquinone and quinhydrone. A subsidiary reaction is that of hydrogen chloride on the quinone present in the form of quinhydrone, the formation of chloroquinol and quinol, and the reaction between the quinol and chloro-*p*-benzoquinone, resulting in the formation of *p*-benzoquinone and chloroquinol.

Hydrogen bromide behaves in a somewhat similar manner, except that the bromo-*p*-benzoquinone can react with hydrogen bromide, forming dibromoquinol.

When saturated solutions of *p*-benzoquinone and chloroquinol or of

chloro-*p*-benzoquinone and quinol are mixed, the precipitate formed consists of nearly pure quinhydrone. The best solvent for the first pair of compounds is water, and for the second pair ether or chloroform.

These results confirm the conclusion drawn by Wichelhaus (Abstr., 1880, 42) that it is impossible to obtain a pure chloroquinhydrone by bringing together quinone and a chlorinated quinol. The products described by Ling and Baker (Trans., 1893, 63, 1314) are mixtures.

When *p*-benzoquinone and chloroquinol are brought together in benzene solution, a chloroquinhydrone is first formed, but when this is heated with the benzene for some time, reaction takes place, and the non-chlorinated quinhydrone is formed on cooling.

Chloro-*p*-benzoquinone has a pale lemon-yellow, and not a yellowish-red, colour. J. J. S.

Quinonoid Compounds. XXVI. *o*-Quinones. Richard Willstätter and Fritz Müller (*Ber.*, 1911, 44, 2171—2181. Compare Abstr., 1908, i, 731).—The following substances have been prepared in the hope of throwing some light on the conditions of equilibrium of the two desmotropic forms of *o*-benzoquinones. The method is that used previously (*loc. cit.*)—rapid oxidation of the corresponding catechol in dry ether by dry silver oxide in the presence of anhydrous sodium sulphate. All of the quinones form stable, deep red crystals, the colourless form being observed only in the case of homo-*o*-benzoquinone; frequently, however, the product of oxidation is obtained in yellow crystals, which are probably mixtures of the red and the colourless modifications. The red forms are shown to be unimolecular. The instability of the colourless forms negatives the suggestion that they may be polymerides; moreover, since they give the reactions of quinones, whilst the bimolecular forms described below do not, it is justifiable to assume that the colourless forms also are unimolecular.

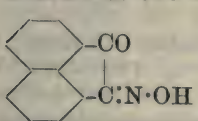
The oxidation of homocatechol under the stated conditions yields *homo*-o-*benzoquinone* [3 : 4-*toluquinone*], $O:C_6H_3Me:O$. Only occasionally, by treating the freshly oxidised solution with petroleum and cooling rapidly in a freezing mixture, have colourless crystals been observed. Usually, by rapid evaporation of the solvent, yellow (mixed) crystals, m. p. 65—67°, are obtained; by recrystallisation they yield the deep red form, m. p. 80—84°, which is more stable than *o*-benzoquinone itself. The substance is readily reduced by cold saturated sulphurous acid. When exposed to sunlight or warmed in ether or acetone, it changes to a *bimolecular* form, $(C_7H_6O_2)_2$, yellow, rhombic prisms, m. p. 124—125°, which has not been depolymerised.

iso*Homo*-o-*benzoquinone* [2 : 3-*toluquinone*], prepared from 2 : 3-dihydroxytoluene, forms unstable dark red prisms and needles, and polymerises, by warming or keeping its ethereal solution, to the *bimolecular* form, m. p. 194—195°, yellow, monoclinic prisms and plates. 3-*Methoxy*-1 : 2-*benzoquinone*, $O:C_6H_3(OMe):O$, m. p. 115—120°, obtained from pyrogallol 1-methyl ether, forms dark red crystals; the stability is such that its solutions in alcohol, water, or dilute sulphuric acid exhibit the reactions of *o*-quinones.

The oxidation of hydroxyquinol by silver oxide yields a quinone which is shown to be *hydroxy*-p-*benzoquinone* by its yellow colour, stability, tendency to form a *quinhydrone* (greenish-black prisms), similarity to the long-known methoxy-*p*-benzoquinone, and difference from 3-methoxy-*o*-benzoquinone. It darkens at 120—124°, and is easily reduced to hydroxyquinol. C. S.

Quinonoid Compounds. XXVII. Chloro-derivatives of Catechol and of *o*-Benzoquinone. RICHARD WILLSTÄTTER and HANS EDUARD MÜLLER (*Ber.*, 1911, **44**, 2182—2191).—Peratoner states that the chlorination of phenols by sulphuryl chloride yields only para-substituted derivatives; with catechol in ether, however, the authors get about 1% of the ortho-isomeride, which is separated by its greater solubility in benzene and its lower b. p. Pure *p*-chlorocatechol has b. p. 136—136·5°/8·5 mm., and a double m. p. It melts at 90—91°; after resolidification, it melts at 59—61°, again becomes solid, and then has m. p. 90° again. The *diacetate* has b. p. 145—147°/7·5 mm., and the *dibenzoate* has m. p. 96—97°. *o*-Chlorocatechol has b. p. 110—111°/11 mm., and m. p. 46—48°; its *dibenzoate* has m. p. 108—109°. 4:5-Dichlorocatechol has m. p. 116—117° (Peratoner and Vitali give 105—106°), and forms a *dibenzoate*, m. p. 140—140·5°. By treating an alcoholic solution of tetrachlorocatechol with water, a *trihydrate*, $C_6Cl_4(OH)_2,3H_2O$, m. p. 94°, is obtained. *o*-Benzoquinone is rapidly dissolved and decolorised by 2% ethereal hydrogen chloride, yielding a mixture of *o*- and *p*-chlorocatechols. 4-*Chloro*-o-*benzoquinone*, m. p. 78° (decomp.), is obtained from *p*-chlorocatechol by the silver oxide method, and crystallises in red needles, which cannot be kept long without decomposing. 3-*Chloro*-o-*benzoquinone*, obtained by oxidising *o*-chlorocatechol with silver oxide or lead peroxide, forms red prisms, which decompose at about 68°. 4:5-*Dichloro*-o-*benzoquinone*, yellow or yellowish-red prisms and plates, m. p. 94° (decomp.), is considerably more stable than the monochlorobenzoquinones. It forms a *quinhydrone*, $C_{12}H_6O_4Cl_4$, glistening, black prisms, decomp. 85°, with the corresponding catechol. The monochloro- and non-halogenated *o*-benzoquinones do not form quinhydrones. C. S.

A New Method for Obtaining Acenaphthenequinone from Acenaphthene. ARNOLD REISSERT (*Ber.*, 1911, **44**, 1749—1752).—A mixture of two isomeric acenaphthenequinone monoximes (annexed constitution) is formed when amyl nitrite (4 mols.) is added to a boiling amyl-alcoholic solution of acenaphthene while a stream of hydrogen chloride is passed through the solution. The amyl alcohol is removed by steam distillation, the oximes extracted with sodium hydroxide solution, and separated by means of their different degrees of acidity. The one oxime is insoluble in hot sodium carbonate solution, and crystallises from glacial acetic acid in soft, faintly yellow crystals, m. p. 207° (decomp.). When the oxime is boiled for some time with glacial acid it yields the isomeric oxime (Francesconi and Pirazzoli, Abstr., 1903, i, 500), which has



m. p. 220°, but then solidifies, and again melts at 290—300°. The quinone can be obtained by hydrolysing the monoxime with 75% sulphuric acid at 100°. J. J. S.

The Catalysis of Borneol and the Catalytic Hydrogenation of Camphor. JULES ALOY and V. BRUSTIER (*Bull. Soc. chim.*, 1911, [iv], 9, 733—735).—The authors have employed the method of Sabatier and Senderens (Abstr., 1905, i, 401) in transforming borneol into camphor. The three metals nickel, iron, and copper have been tried, copper being the best. The optimum temperature is 300°, when the yield is theoretical. Above this temperature, terpene-like products are formed.

The hydrogenation of camphor in the presence of reduced nickel was not successful, but in the presence of this metal, camphoroxime was readily transformed into amines, the secondary amine predominating. W. G.

Hydrogenation of Carvone. GUSTAVE VAVON (*Compt. rend.*, 1911, 153, 68—71. Compare this vol., i, 657).—The reduction of carvone at the ordinary temperature by hydrogen in presence of platinum-black takes place in three stages, corresponding with the formation of carvotanacetone, tetrahydrocarvone, and carvomenthol. This furnishes the most convenient method for preparing *d*-carvotanacetone; the product has b. p. 227—228°, D_4^{18} 0·937, n_D^{18} 1·4817, $[\alpha]_D$ 59·8°. The final stage of the reduction takes place with greater difficulty. W. O. W.

Specific Rotatory Power of Camphor in Acetone Solution. H. MALOSSE (*Compt. rend.*, 1911, 153, 56—57).—The specific rotation of camphor in acetone at different temperatures and concentrations is shown in a tabular statement. The results have been plotted in the form of a curve, and the equations to the different parts of the curve calculated. W. O. W.

The Isomeric Tanacetyl Alcohols. VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 765—769).—By recrystallisation of the hydrogen phthalates of the mixture of alcohols obtained by reduction of tanacetone from the natural oil, and subsequent saponification, the author has isolated a pure *d*-tanacetyl alcohol, and has obtained indications of the presence of the corresponding *l*-compound in the mother liquor. R. V. S.

Some Derivatives of *d*-Tanacetyl Alcohol. VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 769—772).—The tanacetyl alcohol employed had b. p. 206—209°, D^{20} 0·925, n_D 1·4635, $[\alpha]_D$ 69·49°. This was dissolved in light petroleum and treated with sodium, and the sodium derivative produced was added to the calculated quantity of phthalic anhydride in light petroleum. The product is a mixture of several esters, from which by repeated crystallisation a pure *tanacetyl hydrogen phthalate*, $C_{18}H_{22}O_4$, was obtained in tufts of colourless needles, m. p. 120°, $[\alpha]_D + 91·27°$. Its *silver* salt, $C_{18}H_{21}O_4Ag$, has m. p. 85—86°. The *calcium* salt, $(C_{18}H_{21}O_4)_2Ca$, was also prepared.

The *strychnine* salt, $C_{18}H_{21}O_4,C_{21}H_{22}O_2N_2$, has m. p. 177—178°, $[\alpha]_D$ 36·78°.

When the phthalate is saponified with alcoholic potassium hydroxide, d-*tanacetyl alcohol* (β-thujyl alcohol) is obtained. It is an oily liquid, b. p. 206°, D 0·9229, n_D^{16} 1·4625, $[\alpha]_D$ 114·67°. When treated with sodium and phthalic anhydride it regenerates the above-mentioned phthalate, and if it is oxidised with chromic acid it yields a ketone, the semicarbazone of which has all the properties of Wallach's β-tanacetonesemicarbazone (Abstr., 1905, i, 147). R. V. S.

Isoprene from Terpene Hydrocarbons. HERMANN STAUDINGER and HELMUT W. KLEVER (*Ber.*, 1911, **44**, 2212—2215).—By passing the vapour of turpentine through an iron tube at a dark red heat, Tilden obtained a small yield of isoprene, the chief products being hydrocarbons of high b. p. (Trans., 1879, **46**, 417). The yield of isoprene is materially increased by working under diminished pressure, but it can be obtained in 60% yield by passing the vapour of dipentene or limonene, under 20—30 mm. or better still 2—3 mm., over an electrically heated platinum spiral. The isoprene thus obtained is almost pure, and contains very little trimethylethylene; the by-products are gaseous substances (olefines and acetylenes) and hydrocarbons, b. p. 100—150°. Terpinolene, terpinene, and camphene give little or no isoprene under these conditions. C. S.

***iso*Camphane.** PETER LIPP (*Annalen*, 1911, **382**, 265—305).—Camphene has been reduced under varying conditions, and the saturated, dicyclic hydrocarbons, $C_{10}H_{18}$, obtained were oxidised in different ways. The symmetrical, saturated cyclic hydrocarbon corresponding with bornylene should be termed bornylane, but as the name camphane has been generally used in chemical literature for this compound, the term is retained and the unsymmetrical, saturated isomeride is termed *iso*camphane (compare Semmler, *Die Aetherische Oele*, 1906, ii, 62).

Technical camphene obtained from pinene hydrochloride was purified by distillation, and the middle fraction, b. p. 155·5—157°/723 mm., after four crystallisations from aqueous alcohol had m. p. 45° and $[\alpha]_D^{22}$ $-18·94°$. The hydrocarbon was not affected when treated with sodium and boiling ethyl alcohol, but was reduced by Sabatier and Senderens' method, using finely-divided nickel distributed over a pumice surface and kept at 170—190°. After a mixture of hydrogen and the vapour of the hydrocarbon had been passed through the tube three times, the product did not decolorise a chloroform solution of bromine. The product consisted of a mixture of an oily and a solid hydrocarbon. The liquid *iso*camphane is formed in small quantities only, and is probably the reduction product of an impurity (Aschan's pinolene) present in the camphene, as it does not appear to be formed when pure camphene, prepared from *iso*borneol, is used. It has b. p. 160—162°, $[\alpha]_D^{19}$ $+1·15°$ in 10% methyl-alcoholic solution, D^{20} 0·8524, and n_D^{20} 1·45733. The solid isomeride crystallises from methyl alcohol in fern-like masses resembling camphene or ammonium chloride; it has m. p. 65—67° after repeated crystallisation, and is practically inactive. A specimen obtained from pure camphene from

*iso*borneol had m. p. 61·5—63°. The reduction of inactive camphene by Fokin's method (*Zeitsch. angew. Chem.*, 1909, 22, 1496) in ethereal solution and in presence of platinum sponge gave a product with b. p. 164°/713 mm. and m. p. 63—64·5° (corr.). A specimen of *l*-camphene with $[\alpha]_D^{19}$ $-80·7°$ and m. p. 44—44·5° when reduced in a similar manner had b. p. 166—166·5° (corr.)/750 mm. and m. p. 62—63° (corr.) after five crystallisations. The solid *iso*camphane has the consistency of paraffin wax, and in appearance closely resembles camphene; its odour is not quite so pronounced, and it is extremely volatile even at the ordinary temperature. It forms an exception to the generalisation that a saturated compound has a lower b. p. than its unsaturated analogue. It has D_4^{67} 0·82757, n_C 1·43982, n_D 1·44186, and n_G 1·45239 at 67°.

Attempts made to reduce *iso*camphane by means of hydriodic acid and iodine under pressure were unsuccessful; after five hours at 240—250° an isomeric hydrocarbon, $C_{10}H_{18}$, with b. p. 157·5—160·5°, D_4^{20} 0·8344, was obtained, but this was not homogeneous.

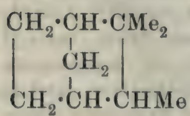
The contradictory statements of Zelinsky (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 768) and Sabatier and Senderens (Abstr., 1901, i, 159; compare Henderson and Pollock, Trans., 1910, 97, 1620) are probably due to the fact that Sabatier and Senderens used an impure specimen of camphene and obtained on reduction a solution of solid *iso*camphane in the liquid isomeride.

Contrary to Sabatier's statement, *iso*camphane is comparatively stable towards oxidising agents. It is most readily oxidised by adding powdered permanganate to a warm 50% acetic acid solution of the hydrocarbon. Among the products are unaltered hydrocarbon (60%), a product containing oxygen and with an odour of camphor, a mixture of camphenilone and camphenilanaldehyde, together with camphenilanic acid and *iso*camphenilanic acid (Bredt and Jagelki, Abstr., 1900, i, 134). A mixture of the calcium salts of the two acids is less soluble in hot than in cold water, although each salt independently is more soluble. *Camphenilanaldehydesemicarbazone*, $C_{11}H_{19}ON_3$, crystallises from dilute alcohol in colourless plates, m. p. 200° (decomp.).

When *iso*camphane is oxidised with nitric acid (D 1·4) for 8·5 hours at 100° under pressure, the products are camphene nitrosite, camphenil nitrite, and camphenilone (compare Jagelki, Abstr., 1899, i, 627), together with resinous compounds.

When the hydrocarbon is boiled for twelve hours with the nitric acid the same products are obtained, and in addition *iso*camphoronic acid and carboxy*apo*camphoric acid (camphoic acid: Marsh and Gardner, Trans., 1896, 69, 74). The normal ammonium salt of the latter acid has m. p. 213—214° (decomp.) (Marsh and Gardner, 198—199°).

The formation of camphenilanic acid and its isomeride indicates that *iso*camphane and camphene have the same ring system, and the annexed structural formula is accepted. The formation of camphoic acid from this hydrocarbon must be accompanied by molecular rearrangement.



The high m. p. for *iso*camphane observed by Vavon (Abstr., 1910, i, 52) is probably due to the presence of camphane. J. J. S.

Constituents of Ethereal Oils. I. Identity of the Aliphatic Terpene from Oil of Hops with Myrcene. II. Methyl Esters of Dicarboxylic Acids. III. Preparation of *iso*Bornylformate. FRIEDRICH W. SEMMLER and ERWIN W. MAYER (*Ber.*, 1911, **44**, 2009—2012).—I. Chapman (Trans., 1903, **83**, 505) has suggested the identity of the aliphatic terpene, $C_{10}H_{16}$, from oil of hops with myrcene. A colourless, mobile, almost odourless oil is now obtained from oil of hops, b. p. 62—63°/17 mm., D^{20} 0·7937, n_D 1·4716. On reduction, a compound identical with dihydromyrcene is obtained, characterised by the crystalline tetrabromide, m. p. 87°. On heating with sulphuric and acetic acids, myrcenol, $C_{10}H_{18}O$, is formed from the hop oil terpene.

II. *Methyl* iso*fenchonecarboxylate*, $C_{12}H_{20}O_4$, has b. p. 131—132°/14 mm., D^{20} 1·0515, n_D 1·4540.

Methyl camphorate has b. p. 137—139°/14 mm. (Brühl and Braunschweig give 155°/15 mm).

Methyl α-tanacetogencarboxylate, $C_{12}H_{20}O_4$, has b. p. 129—130°/15·5 mm., D^{23}_{20} 1·0525, n_D 1·451.

Methyl β-methyladipate has b. p. 122—122·5°/18 mm., D^{20} 1·0372, n_D 1·4336.

III. Camphene when boiled with formic acid yields *iso*bornylformate, $C_{11}H_{20}O_2$, b. p. 91—93°/11 mm., D^{20} 1·005, n_D 1·4726.

E. F. A.

Dimethyldipentene Produced by the Dry Distillation of Dimethylcaoutchouc. A. H. RICHARD (*Compt. rend.*, 1911, **153**, 116—120).—Couturier's βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene behaves, during its polymerisation, exactly like its lower homologue, isoprene. When submitted to the prolonged action of diffused light, it changes into a viscous, bimolecular form, and finally into a white mass having, in physical and chemical properties, a close resemblance to natural rubber. When polymerised by heating at about 150° for some thirty hours, dimethylbutadiene is converted into a viscous liquid, which is separated by distillation with steam into unchanged hydrocarbon and the polymerised product, homocaoutchouc; however long the heating, the reaction seems to be reversible.

By dry distillation, homocaoutchouc yields: (i) βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene, b. p. 69—70°; (ii) a *sesquihomoterpene*, $C_{18}H_{30}$, b. p. 175—180°/22 mm., D^0 0·912; (iii) polyhomoterpenes of higher b. p.; (iv) a *homoterpene*, $C_{12}H_{20}$, b. p. 205° or 97—98°/22 mm, D^0 0·872. The last hydrocarbon should, from analogy to the production of dipentene from isoprene, be *dimethyldipentene*,

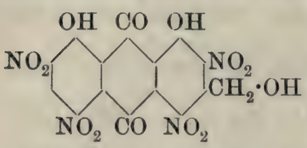
$$CH_2{:}CMe{\cdot}CMe{<}{\begin{matrix}CH_2{\cdot}CMe\\CH_2{-}CH_2\end{matrix}}{>}CMe.$$

Its molecular refraction, calculated from D^{25}_4 0·85322 and n_D 1·47786, agrees well with the formula $C_{12}H_{20}|\overline{}_2$. The substance forms a viscous *tetrabromide* and a *hydrochloronitrosochloride*,

$$C_{12}H_{20},NOCl,HCl,$$

a yellow powder, decomp. 160°, and by reduction with hydrogen and platinum-black yields a *hydrocarbon*, $C_{12}H_{22}$, b. p. 93—95°/20 mm., D_4^{25} 0·842307, and n_D 1·46635. C. S.

Constitution of Nitro-compounds Obtained by the Action of Nitric Acid on Aloins. EUGÈNE LÉGER (*Compt. rend.*, 1911, **153**, 114—116).—The author has shown previously that barbaloin and *iso*barbaloin are converted by nitric acid into a tetranitroaloemodin, which yields chrysammic acid and 2 : 4 : 6-trinitro-*m*-hydroxybenzoic acid by further treatment with nitric acid. Experiments are described now to prove that the trinitro-*m*-hydroxybenzoic acid is formed, not independently of the tetranitroaloemodin, but at the expense of some of the chrysammic acid. Assuming that Robinson and Simonsen's constitution (Trans., 1909, **95**, 1088) of the latter is correct, and remembering that the majority of the compounds obtained from the aloins are derivatives of β-methylanthraquinone, it follows that tetranitroaloemodin must be represented by the annexed constitution.



Since the aloins are glucosides of aloemodin and *d*-arabinose, the author is of opinion that the arabinose molecule is attached to the phenolic hydroxyl group in position 1 in barbaloin, and to the phenolic hydroxyl group in position 8 in *iso*barbaloin. C. S.

Glucosides from the Leaves of Digitalis purpurea. F. KRAFT (*Schweiz. Wochensch. Chem. Pharm.*, 1911, Nos. 12, 13, 17; Reprint, 9 pp.).—*Gitalin*, m. p. 150—155°, obtained from the cold aqueous extract of *Digitalis* leaves by means of chloroform, is a white, amorphous glucoside of neutral reaction, which is soluble in 600 parts of cold water. It is soluble in most of the usual solvents, but the solutions decompose more or less quickly. By the addition of water to its alcoholic solution, the glucoside is converted into crystalline *gitalin hydrate*, m. p. 75°, which is soluble in about 3000 parts of water.

The decomposition of gitalin in solution is accomplished best by the evaporation of an alcoholic solution in a vacuum, whereby *anhydrogitalin*, m. p. 255°, a crystalline glucoside quite insoluble in water, is obtained. Anhydrogitalin is hydrolysed by alcohol and 10% hydrochloric acid on the water-bath, yielding *anhydrogitaligenin*, m. p. 119° (which closely resembles anhydrodigitoxigenin), and two sugars, Kiliani's digitoxose and another, which is not crystallisable.

The literature of digitoxin is very confused. The digitoxin obtained by Keller is claimed by Burmann to be identical with his ψ-digitoxin (which appears to be identical with gitalin). This cannot be so, because Keller's digitoxin is insoluble in water. The author states that gitalin, in the form of its hydrate or of anhydrogitalin, is the chief constituent, not only of Keller's, but of all commercial, digitoxins.

Digitalinum verum was obtained by Kiliani from the seeds of *Digitalinum germanicum*; it is also present in minute amount in the leaves.

Confusion has also arisen in the literature from the fact that the

name digitonin is given to two substances, Schmiedeberg's amorphous glucoside, and Kiliani's crystalline, inactive glucoside. The author retains the name for the latter, and calls the former digitsaponin. From the dilute alcoholic extract of digitalis leaves he obtained an inactive *glucoside*, m. p. 265° (decomp.), which he regarded at first as identical with digitonin; a direct comparison of the two substances, however, shows that they differ in many important properties. By hydrolysis digitsaponin yields amorphous sapogenins and two sugars, one of which is a pentose, the other dextrose. C. S.

Phloridzin- and Phloretin-glycuronic Acids. JOS. SCHÜLLER (*Zeitsch. Biol.*, 1911, 38, 274—308).—See this vol., ii, 814.

Action of Light of Mercury Lamp on Solutions of Chlorophyll. HENRI BIERRY and J. LARGUIER DES BANCELS (*Compt. rend.*, 1911, 153, 124—125).—Alcoholic solutions of chlorophyll (from spinach) in quartz vessels are exposed to the light of two mercury vapour lamps for twenty-four to forty-eight hours. The solutions become faintly yellow, and no longer show the absorption bands characteristic of chlorophyll. Tests for urobilinogen were applied, with positive results. A benzene solution of chlorophyll becomes colourless under the same conditions, but does not show the colour reactions of urobilinogen. C. S.

Chemical Nature of *allo*-Chlorophyll. LEON MARCHLEWSKI and J. MARSZAŁEK (*Ber.*, 1911, 44, 1705—1708. Compare Malarski and Marchlewski, Abstr., 1910, i, 692).—*allo*-Chlorophyllan can be obtained in appreciable amounts from maple leaves: thus, 20 grams of crude chlorophyllan gave 5·76 grams of the *allo*-compound. The compound contains 3% of methoxyl, and prolonged treatment with zinc hydroxide tends to diminish the percentage; it also yields 31·8% of phytol, and when heated at 105° its properties change. The *allo*-chlorophyllanic acids, obtained by hydrolysing the product dried at 105°, are insoluble in ether. The acids have a cherry-red colour, whilst chlorophyllanic acids are olive-green.

With zinc acetate, *allo*-chlorophyllan yields a zinc derivative, zinc *allo*-chlorophyll, similar to zinc chlorophyll, but with a different absorption spectrum. It is questionable whether *allo*-chlorophyll yields phylloporphyrin, but it is suggested that it contains two carboxyl groups, one present as methyl, and the other as phytyl, ester.

J. J. S.

The Chlorophyll Group. X. Phyllohæmin. II. LEON MARCHLEWSKI and J. ROBEL (*Biochem. Zeitsch.*, 1911, 34, 275—279).—Phyllohæmin was prepared by treatment of phylloporphyrin in warm acetic acid saturated with sodium chloride with permanganate. The substance which separated, after washing free from excess of sodium chloride and iron salt, was recrystallised by Schalféeff's method, that is, by dissolving in chloroform containing quinine, throwing the solution into acetic acid saturated with sodium chloride and kept at 90°, and allowing the mixture to cool. The measurement

of the spectral bands and other properties showed a marked similarity between this preparation and the blood-hæmin. S. B. S.

Quinonoid Compounds. XXV. Aniline Black. V. RICHARD WILLSTÄTTER and CARL CRAMER (*Ber.*, 1911, **44**, 2162—2171. Compare Abstr., 1909, i, 535, 975).—A criticism of Green and Woodhead's paper (Trans., 1910, **97**, 2388). These authors agree with Willstätter and Dorogi (*loc. cit.*) that the oxidation products of aniline are derivatives of the leuco-base,

$$NHPh\cdot[C_6H_4\cdot NH]_6\cdot C_6H_4\cdot NH_2,$$

but dispute most of their other statements. The chief cause of Green and Woodhead's diverging views which the authors consider erroneous, is the fact that the substance which they have regarded as the leuco-base, $C_{48}H_{42}N_8$, and have obtained by reducing emeraldine with titanium trichloride, is in reality the monoquinonoid black, $C_{48}H_{40}N_8$. The real facts are as follows: Monoquinonoid black, $C_{48}H_{40}N_8$, is obtained by reducing triquinonoid black (emeraldine) with titanium trichloride in the cold, or, better, with phenylhydrazine at 100°. Diquinonoid black, $C_{48}H_{38}N_8$, is easily obtained pure by the spontaneous oxidation of monoquinonoid black or of the leuco-base in the air. Triquinonoid black (emeraldine), $C_{48}H_{36}N_8$, is obtained by oxidising an excess of aniline salt with dichromate, persulphate, chlorate, or other agents. Tetraquinonoid black (nigraniline), $C_{48}H_{34}N_8$, is obtained best by oxidising triquinonoid black with hydrogen peroxide. (By oxidation with dichromate or persulphate, an oxygenated pentaquinonoid black, $C_{48}H_{33}ON_7$, stable to sulphurous acid, is obtained.) All these quinonoid blacks yield the first-mentioned monoquinonoid black by oxidation by Knecht's titanium trichloride process, in the cold or at 90°. The true leuco-base, $C_{48}H_{42}N_8$, is obtained by treating any of these blacks with phenylhydrazine at 150°. (A black which contains iron in its ash must be first boiled with 2*N*-sulphuric acid, otherwise the reaction with phenylhydrazine above 100° proceeds explosively.)

Green and Woodhead state that the salts of nigraniline are very unstable, changing slowly in the cold, rapidly by warming, to emeraldine and *p*-benzoquinone. On the contrary, the authors find that the only change produced by 17% sulphuric acid at 200° is the quantitative hydrolysis of one quinoneimine group.

Green and Woodhead also state that the emeraldine and nigraniline dissolve easily and completely in 80% acetic acid or in 60% formic acid. This, again, is incorrect; only suspensions are obtained.

C. S.

Action of Oxidising Agents on *iso*Pyromucic Acid. Dialdehydes of Dibromomaleic and Bromohydroxymaleic Acids. G. CHAVANNE (*Compt. rend.*, 1911, **153**, 185—188*).—The constitution of *iso*pyromucic acid previously determined by the author (Abstr., 1905, i, 77), and confirmed by Blaise and Gault (Abstr., 1909, i, 134), is supported by a study of the products of oxidation. Most oxidising agents act too energetically, but hydrogen peroxide in

* and *Bull. Soc. chim. Belg.*, 1911, **25**, 264—279.

alkaline solution at the ordinary temperature produces maleic acid carbon dioxide, and a little formic acid.

It has been shown (*loc. cit.*) that the action of bromine and water on *iso*pyromucic acid yields, under apparently identical conditions, either a substance, $C_5H_4O_4Br_2$, decomp. 104—105°, or a substance, $C_4H_2O_2Br_2$, m. p. 34°. These substances can now be obtained at will. *iso*Bromopyromucic acid forms with bromine an additive *compound*, $C_5H_3O_3Br_3$, large prisms, m. p. 88—89°, which is decomposed by ice water, yielding hydrogen bromide and the substance $C_5H_4O_4Br_2$ previously described (it decomposes at 175° when pure). All attempts to obtain the substance $C_4H_2O_2Br_2$ from the substance $C_5H_4O_4Br_2$ have failed. However, by dissolving the additive compound $C_5H_3O_3Br_3$ in bromine (1 mol.) and adding the solution to a little water at the ordinary temperature, the substance $C_4H_2O_2Br_2$, m. p. 34°, is obtained in good yield. There is no doubt that it is dibromomaleic dialdehyde, because: (i) by oxidation with bromine and water under suitable conditions it gives an almost theoretical yield of bromomucic acid, and (ii) when heated with a large excess of water it decomposes into hydrogen bromide and a *substance*, $C_4H_3O_3Br$, m. p. 83—83·5°, which has acidic properties, forms an *acetyl* derivative, b. p. 118—120°/1·5 mm., *semicarbazone*, decomp. 198°, *phenylhydrazone*, decomp. 126—126·5°, and *trioxime*, decomp. 94—95°, reduces ammoniacal silver nitrate, gives Schiff's test, and is oxidised by bromine and water chiefly to bromomucic acid. The substance, therefore, is α-bromo-β-hydroxymaleic dialdehyde, which reacts in the tautomeric forms: CHO·C(OH):CBr·CHO and CHO·CO·CHBr·CHO.

C. S.

Action of Halogen Acids on Hydroxyarylxanthenols. Moses Gomberg and C. J. West (*J. Amer. Chem. Soc.*, 1911, 33, 1211—1213).—Many investigators have examined the action of acids on hydroxyarylxanthenols, and report generally that coloured oxonium salts are formed. The authors have made a systematic study of the reaction (as an introduction to the study of the constitutions of fluoran, fluorescein, etc.), and find that, in general, hydroxy- and methoxy-xanthenols yield colourless carbinol chlorides, which tautomerise with extreme readiness to coloured quinocarbonium salts in the presence of excess of acid (compare Gomberg and Cone, Abstr., 1910, i, 55, 869). When one of the two phenyl groups in the xanthone ring contains a hydroxyl group in the para-position to the carbinol carbon atom, the colourless carbinol halide changes spontaneously, even in the absence of excess of acid, to the coloured quinocarbonium salt. Full information is promised in a later paper.

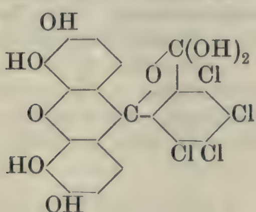
C. S.

Tetrachlorogallein and Some of its Derivatives. II. William R. Orndorff and T. G. Delbridge (*Amer. Chem. J.*, 1911, 46, 1—55. Compare Abstr., 1909, i, 733).—A more convenient method of preparing the coloured tetrachlorogallein hydrate is described, in which tetrachlorophthalic acid, pyrogallol, and zinc chloride are heated at 200° in a current of carbon dioxide.

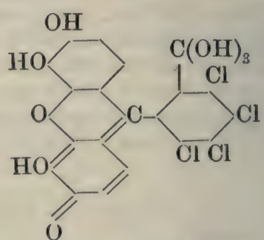
The authors have extended their investigations of the coloured

and the colourless derivatives of tetrachlorogallein by the isolation of a colourless tetrachlorogallein hydrate, a colourless tetrachlorogalleincarbinolcarboxylic acid, and two colourless solvates, the diacetonate and the etherate. All colourless derivatives receive a lactonoid constitution, whilst the coloured compounds are represented as quinonoid.

Colourless *tetrachlorogallein hydrate*, $C_{20}H_8O_7Cl_4,H_2O$, is obtained by adding water to an acetone solution of the red hydrate, and passing moist carbon dioxide through the solution; after several days the colourless hydrate crystallises in triclinic needles. Chemically its behaviour is almost identical with that of the red hydrate. It loses H_2O at 157°, and forms tetrachlorogallein. Both hydrates react with dry ammonia to form the same bluish-black *tetra-ammonium* salt as does tetrachlorogallein itself, but whilst the red hydrate absorbs hydrogen chloride to form a red *hydrochloride*, $C_{20}H_8O_7Cl_4,HCl,H_2O$, without loss of water, the colourless hydrate slowly absorbs hydrogen chloride and also loses 1 mol. H_2O, yielding the red hydrochloride, $C_{20}H_8O_7Cl_4,HCl$, identical with that produced from tetrachlorogallein (*loc. cit.*). This difference in behaviour strikingly confirms the constitutions ascribed to the two hydrates:

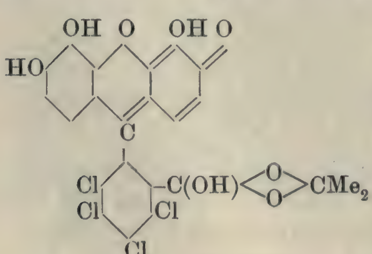


Colourless hydrate.



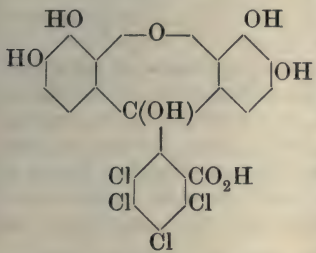
Coloured hydrate.

Tetrachlorogallein diacetonate, $C_{20}H_8O_7Cl_4,2C_3H_6O$, separates in almost colourless crystals from a solution of tetrachlorogallein in dry acetone. It loses acetone in a vacuum over phosphoric oxide, gradually becoming intensely red, and finally, after being heated at 157° in carbon dioxide, colourless again, yielding tetrachlorogallein; the colour is most intense when the composition of the decomposing diacetonate, corresponds with the formula $C_{20}H_8O_7Cl_4,C_3H_6O$. In the air the diacetonate loses its acetone and takes up rather more than one molecule of water to form a mixture of red tetrachlorogallein hydrate with a little of the carbinolcarboxylic acid (see below). The behaviour of the diacetonate accords with the annexed constitution.



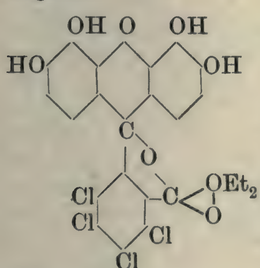
Tetrachlorogalleincarbinolcarboxylic acid, $C_{20}H_{10}O_8Cl_4,H_2O$, is obtained as a white precipitate by adding a cold acetone solution of the preceding diacetonate (or of either of the hydrates or of anhydrous

tetrachlorogallein itself) to a large excess of cold acidified water. The substance loses H_2O at 157°, yielding the colourless, anhydrous *carbinolcarboxylic acid* (annexed constitution), which differs from



the isomeric red hydrate in that it does not lose more water even at 203°. However, it combines very easily with hydrogen chloride in the cold, forming a red *hydrochloride* (probably the hydrochloride obtained from the red tetrachlorogallein hydrate, since it loses water and hydrogen chloride at 157°, yielding tetrachlorogallein), and with dry ammonia, forming by loss of water the bluish-black tetra-ammonium salt described above. This confirms Baeyer's statements that all carbinols are colourless, and that colour only appears in consequence of loss of water.

Attempts to crystallise tetrachlorogalleincarbinolcarboxylic acid give a mixture of the colourless and the coloured tetrachlorogallein hydrates; also the action of acetic anhydride produces the colourless tetrachlorogallein tetra-acetate, thus showing that the elimination of water from the carbinol acid does not necessarily give a coloured compound.



When tetrachlorogallein diacetonate is shaken with dry ether and filtered, the filtrate yields a colourless *etherate*,

$$C_{20}H_8O_7Cl_4,C_4H_{10}O,$$

which loses ether extremely easily, and at 157° in carbon dioxide yields a mixture of equal parts of tetrachlorogallein and its carbinolcarboxylic acid. The etherate becomes pink in air, owing to its conversion, by absorption of water and loss of ether, into colourless tetrachlorogallein hydrate, the carbinolcarboxylic acid, and a little of the coloured hydrate. The etherate is given the annexed constitution. C. S.

New Synthesis of Trihydroxythioxanthones. FRITZ ULLMANN and MASUO SONE (*Ber.*, 1911, 44, 2146—2148).—When warmed gently with concentrated sulphuric acid, aromatic mercaptans and gallic acid readily condense to form trihydroxythioxanthones. Gallic acid and phenyl mercaptan yield Davis and Smiles' 2 : 3 : 4-trihydroxythioxanthone (Trans., 1910, 97, 1290), the *trimethyl ether* of which has m. p. 153—154°. Gallic acid and *p*-tolyl mercaptan yield 2 : 3 : 4-*trihydroxy-7-methylthioxanthone*, $C_6H_3Me{<}{}^{CO}_{-S-}{>}C_6H(OH)_3$, yellow needles, darkening above 240°. It forms a reddish-brown solution in dilute alkalis, an orange solution with a faint green fluorescence in concentrated sulphuric acid, and yields with methyl sulphate and potassium hydroxide a *trimethyl ether*, yellow needles, m. p. 135°.

C. S.

Oxythiophens. MAURICE LANFRY (*Compt. rend.*, 1911, 153, 73—76).—When thiophen is boiled with hydrogen peroxide (6—13 vols.) two substances are obtained, and may be separated by fractionation. *Dioxythiophen*, $C_4H_4O_2S$, has b. p. about 130°, D^{20} 1·26; *tetraoxythiophen*, $C_4H_4O_4S$, has b. p. 158—160°, D^{20} 1·43. The compounds closely resemble one another, and show no phenolic properties; they are colourless liquids with an agreeable odour, unaltered by treatment with sodium, alkali hydroxide, or phenylhydrazine. Nitric or sulphuric acid brings about profound decomposition on boiling. With concentrated sulphuric acid and isatin, they develop a green coloration, destroyed by excess of water. Tetraoxythiophen forms an *octabromide*, $C_4O_4SBr_8$, m. p. 65—66°, by addition and substitution; the existence of this compound indicates that the oxygen in the original substance is united to sulphur.

When the amount of active oxygen in the hydrogen peroxide corresponds with less than 1·5 grams per gram of thiophen, a brown substance is formed, soluble in alkalis. It appears to be a mixture, and under some conditions approximates in composition to the formula $(C_4H_2OS)_n$. W. O. W.

Action of Carbon Disulphide and Potassium Hydroxide on *p*-Tolyl Methyl Ketone and α-Thienyl Methyl Ketone. C. KELBER and A. SCHWARZ (*Ber.*, 1911, 44, 1693—1700. Compare Abstr., 1892, 340, 1127; 1904, i, 510; 1905, i, 810; 1909, i, 46, 47).—*p*-Tolyl methyl ketone and α-thienyl methyl ketone react with carbon disulphide and alkali in much the same manner as acetophenone (Abstr., 1910, i, 390), the products having the characteristics of thiols.

The *compound*, $C_{10}H_{10}OS_2 = C_6H_4Me{\cdot}CO{\cdot}CH{:}C(SH)_2$, obtained from *p*-tolyl methyl ketone, carbon disulphide, finely-powdered potassium hydroxide, and two drops of water by heating on the water-bath and then cooling rapidly, crystallises from light petroleum in glistening, yellow plates, m. p. 84—85°. Carbon dioxide precipitates it from solutions of its alkali salts. The *dimethyl ether*, $C_{12}H_{14}OS_2$, forms pale yellow, glistening needles, m. p. 104—105°; the *dibenzyl ether*, $C_{24}H_{22}OS_2$, broad, yellow needles, m. p. 111·5—112·5°, and the *dibenzoyl* derivative, $C_{24}H_{18}O_3S_2$, pale yellow crystals, m. p. 125°. When heated for four hours at 125° with 0·5*N*-alcoholic potassium hydroxide, the product yields hydrogen sulphide and *p*-toluic acid. Alcoholic ammonia at 140° yields ammonium thiocyanate and *p*-tolyl methyl ketone, and alcoholic hydrochloric acid at 125° yields ethyl mercaptan and *p*-tolyl methyl ketone. When heated on the water-bath with aniline, the product yields a *compound*,

$$C_6H_4Me{\cdot}CO{\cdot}CH{:}C(SH){\cdot}NHPh\ (?),$$

which crystallises from light petroleum in needles, m. p. 80·5—81·5°, and is readily soluble in alkalis. After prolonged heating with aniline, a *compound*, crystallising in red needles, m. p. 192·5—193°, is formed (N = 8·28%).

The *product*, $C_7H_6OS_3$, obtained from α-thienyl methyl ketone, crystallises from light petroleum in yellow plates, m. p. 90—91°. The *dimethyl ether*, $C_9H_{10}OS_3$, forms compact, yellow needles, m. p. 96·5°, and the *dibenzoyl* derivative, $C_{21}H_{14}O_3S_3$, slender, felted, yellow needles, m. p. 118·5°. Its behaviour towards alcoholic solutions of potassium

hydroxide, ammonia, and hydrochloric acid is exactly analogous to the behaviour of the product from *p*-tolyl methyl ketone with these reagents.

The *ethylene ether* of the product previously described (Abstr., 1910, i, 391), $COPh\cdot CH\colon C<\begin{matrix} S\cdot CH_2 \\ | \\ S\cdot CH_2 \end{matrix}$, crystallises from light petroleum in long, pale yellow needles, m. p. 80°. Its solution in concentrated nitric acid has a blue to cherry-red colour, and that in concentrated sulphuric acid a deep yellow colour. When reduced with zinc dust and sodium hydroxide solution, the ether yields propiophenone, detected by means of its semicarbazone and ethylene mercaptan,

$$COPh\cdot CH\colon CS_2C_2H_4 + 6H = COPh\cdot CH_2Me + C_2H_4(SH)_2.$$

The *propylene ether*, $COPh\cdot CH\colon CS_2C_3H_6$, m. p. 52—53°, is reduced in an exactly similar manner, and these reactions are used as an argument in favour of the unsaturated dithiol structure previously given to the condensation product from acetophenone. J. J. S.

Cinchona Alkaloids. XIII. Fluorescence Phenomena with Cinchona Alkaloids. PAUL RABE and OSWALD MARSCHALL (*Annalen*, 1911, **382**, 360—364. Compare Stokes, *Jahresber.*, 1864, 100).—The phenomena of fluorescence of cinchona alkaloids have been examined qualitatively in order to establish relationships between constitution and fluorescence. The experiments were made with sunlight, light from a uviol lamp, and the ultra-violet rays from an arc lamp. The general method adopted was similar to that used by Tswett (Abstr., 1901, ii, 298; compare also Stobbe, *ibid.*, 1909, ii, 282).

The results show that slight differences in arrangement of the atoms within the molecule, as exemplified by cases of stereoisomerism, produce an appreciable effect on the fluorescence; the examples quoted are the following pairs of substances, which were examined in the solid form by filtered ultra-violet light: cinchonine, blue; cinchonidine, pale blue; quinine, intense blue; quinidine, light blue; quinine hydrochloride, intense blue; quinidine hydrochloride, yellowish-red; deoxyquinine, reddish-blue; deoxyquinidine, sky-blue.

In all cases the fluorescence is more pronounced when working with ultra-violet light than with sunlight; the quality and intensity of the fluorescence varies with the solvent, but no generalisations can be drawn between the two. When water is added gradually to an alcoholic solution, it frequently first produces an increase and ultimately a diminution of the fluorescence.

With quinine salts an important factor is the acid with which the base is combined; thus, when 0·1 gram of the base is dissolved in 20 c.c. of $0{\cdot}1N$-acid, the following results are obtained: sulphuric, nitric, phosphoric, hydrofluoric, and trichloroacetic give strongly fluorescent solutions, tartaric and acetic moderately strongly fluorescent, and the halogen hydracids very feebly fluorescent solutions.

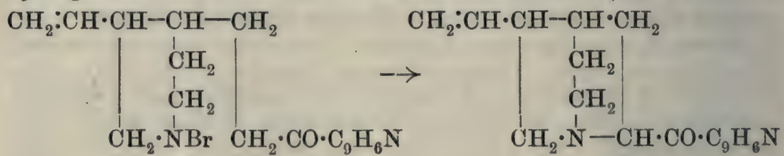
J. J. S.

Cinchona Alkaloids. XIV. Decomposition of Oximinoquinotoxine. PAUL RABE and ERNST MILARCH (*Annalen*, 1911, **382**, 365—368. Compare Rabe and Ackermann, Abstr., 1907, i, 546).—The products obtained by shaking phosphorus pentachloride with an

ice-cold chloroform solution of oximinoquinotoxine (Rohde and Schwab, Abstr., 1905, i, 228) and then pouring on to ice and water are quinic acid and the nitrile of meroquinine. The oximino-derivative of the tertiary methylquinotoxine behaves in a similar manner, yielding quinic acid and the nitrile of *N*-methylmeroquinine (Rabe and Ritter, Abstr., 1905, i, 811). J. J. S.

Cinchona Alkaloids. XV. Partial Synthesis of Cinchonine. Paul Rabe (*Ber.*, 1911, 44, 2088—2091).—An account of the transformation of cinchotoxine into cinchonine.

N-*Bromocinchotoxine* (I), obtained by the action of aqueous sodium hypobromite on cinchotoxine in dilute hydrochloric acid solution at the ordinary temperature, crystallises from alcohol or ether in colourless, elongated prisms, m. p. 153°. It differs from cinchotoxine in being without action towards litmus and methyl iodide. When treated in hot alcoholic solution with sodium ethoxide, it loses hydrogen bromide, and is converted into cinchoninone (II):



(I.) (II.)

The reduction of cinchoninone to cinchonine has been described previously (Rabe and Buchholz, Abstr., 1908, i, 100). F. B.

Ephedrine and ψ-Ephedrine. Ernst Schmidt [with W. Calliess] (*Apoth. Zeit.*, 1911, No. 37; Reprint 3 pp.).—A preliminary note necessitated by work published by Emde, Fourneau, and Rabe and Hallensleben (compare this vol., i, 396). The synthesis of a base isomeric with ephedrine or ψ-ephedrine starts from phenyl α-bromoethyl ketone. This is converted into *phenyl-α-aminoethyl ketone*, NH_2·CHMe·COPh (*hydrochloride*, m. p. 179°; *nitrate*, m. p. 139—140°; *picrate*, m. p. 160°; *platinichloride*, m. p. 200°; *aurichloride*, m. p. 151°; *mercurichloride*, m. p. 126° or 165°; *stannichloride*, m. p. 219—220°), which is reduced by sodium amalgam in faintly acid solution at 0° to *phenyl-α-aminoethylcarbinol*,

NH_2·CHMe·CHPh·OH

(*hydrochloride*, m. p. 165°; *aurichloride*, m. p. 130°; *platinichloride*, m. p. 187—188°). This carbinol forms by direct methylation a quaternary base, an aqueous solution of which, by distillation, yields trimethylamine and an oily substance free from nitrogen. The substance NHMe·CHMe·CHPh·OH is obtained by treating phenyl α-bromoethyl ketone with methylamine and reducing the product with sodium amalgam in faintly acid solution.

ω-Aminobenzyl methyl ketone yields by reduction the *carbinol*, NH_2·CHPh·CHMe·OH (*hydrochloride*, m. p. 165—167°), which reacts with methyl iodide in methyl alcohol to form, ultimately, a quaternary base, the distillation of which yields trimethylamine and an oil, as yet unexamined. ω-Bromobenzyl methyl ketone and

methylamine yield a *base*, NHMe·CHPh·COMe (*hydrochloride*, m. p. above 200°), which is converted by reduction into *ω-methylaminobenzylmethylcarbinol*, NHMe·CHPh·CHMe·OH, an oil the *hydrochloride* of which has m. p. 190°. C. S.

d-Lupanine. AUGUST BECKEL (*Arch. Pharm.*, 1911, **249**, 329—353).—A chemical relationship between lupanine, $C_{15}H_{24}ON_2$, and sparteine, $C_{15}H_{26}N_2$, has often been assumed in consequence of the similarity in composition and the occurrence of both alkaloids in the seeds of lupines. The two nitrogen atoms in sparteine are tertiary, and the alkaloid behaves as a diacidic base and forms two isomeric methiodides. The author has examined very thoroughly the behaviour of *d*-lupanine (isolated as the hydrochloride from the seeds of *Lupinus angustifolius*) with methyl iodide, with and without a solvent, at the ordinary temperature, at 100°, and even at 190°, but in no circumstances has a methiodide been isolated other than that described in the literature (m. p. 240°, decomp.); their interaction at 150° results in a partial, at 190° in a complete, conversion of the methiodide into lupanine hydriodide. Lupanine methiodide does not form an additive compound with hydriodic acid. Lupanine an ethyl iodide, alone or in boiling alcohol, yield lupanine hydriodide. Benzyl bromide, but not benzyl chloride, forms an additive compound with lupanine, which is isolated as the *aurichloride*,

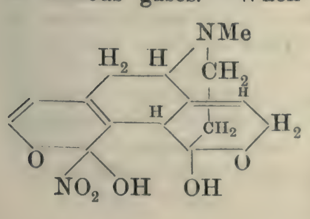
$$C_{15}H_{24}ON_2 \cdot CH_2Ph,AuCl_4,$$

m. p. 186—187° (decomp.) (*platinichloride*, m. p. 203—204°, decomp.). Lupanine methiodide does not react with ethyl iodide or benzyl bromide at the ordinary temperature or at 100°.

d-Lupanine does not decolorise acidified potassium permanganate, and can be titrated as a mono-acidic base. C. S.

Morphine. I. HEINRICH WIELAND and PAUL KAPPELMEIER (*Annalen*, 1911, **382**, 306—339).—Knorr's formula for morphine is discussed. Most of the methods used in connexion with the elucidation of the constitution of morphine have been based on Hofmann's degradation process involving a rupture of the nitrogen ring. The author has attempted to use the process of oxidation, but it has not been found possible to obtain definite homogeneous products by direct oxidation. Attempts to obtain acids from 2-nitrosomorphine by hydrolysing to the 2:3-quinone and subsequent oxidation also proved unsuccessful. The oxidation of 2-amino- and 2-hydroxy-morphine also gave negative results.

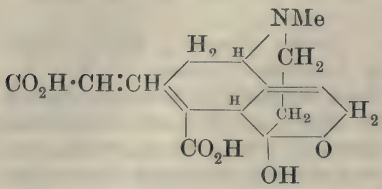
It has been found possible to rupture the morphine ring by means of nitrous gases. When these gases are passed into an aqueous



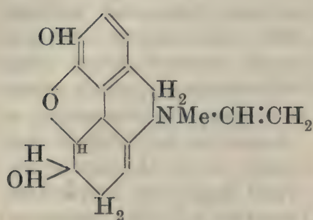
solution of a morphine salt, 2-nitrosomorphine is formed together with the unstable nitrate of a base, $C_{17}H_{18}O_6N_2$. The annexed structural formula suggested for the base is that of a quinnitrole (Zincke, Abstr., 1905, i, 881). The reaction consists in the addition of nitric acid to one ring, of the hydro-

lytic rupture of the oxygen bridge and the oxidation of the secondary alcoholic group to a ketonic group.

When an aqueous solution of the unstable nitrate is warmed, a 30% yield of the colourless nitrate of the base $C_{17}H_{19}O_6N$ is obtained. This compound has acidic properties, is termed morphinic acid, and is regarded as formed by the oxidation of the *o*-quinone, from which the quinnitrole is derived, and is therefore represented by the annexed formula.



The adjacent structural formula for morphine is suggested. According to this the nitrogen atom is attached to carbon atom 9 of the phenanthrene nucleus, but contains a free vinyl group. The actual ring formation occurs with the aid of this vinyl group in the conversion of morphine into methylmorphimethine, *apo*morphine, thebenine, etc. This formula accounts for the readiness with which many morphine derivatives combine with water, and also for the readiness with which the $-N\cdot C\cdot C-$ group is eliminated from morphine.



The compound described by Mayer (*Ber.*, 1871, **4**, 121) as nitrosomorphine is probably morphine nitrite, and differs entirely from 2-*nitrosomorphine*, which is formed when nitrous fumes are passed into a suspension of morphine hydrochloride in water at $-2°$ to $-3°$; the salt dissolves gradually, the liquid turns orange-red, and the nitroso-compound can be isolated as its *sodium* derivative, $C_{17}H_{17}O_4N_2Na,H_2O$, by the addition of cold 20% sodium hydroxide solution. This derivative crystallises from 90% alcohol in brilliant, dark red needles, and turns black when heated, but has no definite m. p. The *silver* derivative forms an insoluble, almost black precipitate, m. p. 181—182° (decomp.), but does not react with methyl iodide. The *hydrochloride*,

$$C_{17}H_{18}O_4N_2,HCl,$$

forms lemon-yellow needles, m. p. 248° (decomp.). 2-Nitrosomorphine, $C_{17}H_{18}O_4N_2,H_2O$, obtained by the action of acetic acid on the sodium derivative or of ammonia on the hydrochloride, crystallises from boiling alcohol in polymorphous forms; the more stable form consists of slender, dark orange-red needles, m. p. 225° (decomp.). It reduces neither Fehling's solution nor ammoniacal silver nitrate, is not appreciably decomposed by acids or alkalis, and its alkali salts give a dark green coloration with ferric chloride. The minutest traces of morphine react with a drop of sodium nitrite solution, yielding a yellow coloration which turns to orange on the addition of alkali, and the reaction is an extremely delicate one for detecting morphine. When reduced with tin and hydrochloric acid, the nitroso-compound yields 2-*aminomorphine*, $C_{17}H_{20}O_3N_2,H_2O$, which forms colourless, glistening crystals or quadratic plates, m. p. 258°. The *hydrochloride*,

$C_{17}H_{20}O_3N_2,2HCl$, is readily soluble in water, and has $[\alpha]_D$ $-90°$; the *picrate* forms yellow needles, decomposing at 172°.

The amino-compound is readily diazotised, yielding an *o-diazo-anhydride*; the *hydrochloride*, $C_{17}H_{17}O_3N_3,HCl$, is formed when the amino-compound is suspended in alcohol, treated with alcoholic hydrogen chloride and ethyl nitrite, and precipitated by the addition of ether. The dry salt decomposes at 98°. When warmed with alcohol, the diazo-compound regenerates morphine, but it has not been found possible to obtain pure 2-hydroxymorphine.

Morphine as a phenol couples with diazonium salts, yielding azo-dyes. *Benzeneazomorphine*, $C_{23}H_{23}O_3N_3$, crystallises from alcohol in slender, orange-yellow needles, m. p. 175° (decomp.). Its solutions in acids are orange-brown, and in alkali, blood-red. When reduced with stannous chloride and hydrochloric acid, it yields aniline and amino-morphine.

2-*Aminocodeine*, $C_{18}H_{22}O_3N_2$, obtained by reducing the corresponding nitro-derivative, crystallises from absolute alcohol, has m. p. 226°, and does not possess reducing properties. Its *hydrochloride* is amorphous, and is readily diazotised to a diazonium salt, which couples with an alkaline solution of β-naphthol, yielding a brilliant red dye. When a solution of the diazonium salt is heated, small amounts of 2-*hydroxy-codeine*, $C_{18}H_{21}O_4N$, are obtained in colourless needles, m. p. 176°.

2-Nitroso- and 2-amino-morphine are readily transformed into the corresponding *apo*morphine compounds by the loss of water, for example, when heated with 30% hydrochloric acid at 145° and 130° respectively. 2-*Nitroso*apo*morphine hydrochloride*, $C_{17}H_{16}O_3N_2,HCl$, crystallises from hot water in felted, yellowish-green needles, changes colour at 200°, but has no definite melting point, and reduces ammoniacal silver nitrate, but not Fehling's solution. The free *base*, $C_{17}H_{16}O_3N_2,H_2O$, crystallises from absolute alcohol in red needles, which are not molten at 300°. 2-*Amino*apo*morphine hydrochloride*, $C_{17}H_{18}O_2N_2,2HCl$, crystallises from dilute hydrochloric acid in colourless, felted needles, m. p. 260—265°. It reduces hot Fehling's solution, and with ferric chloride gives a deep violet coloration, which is rapidly transformed to an olive-green. The *base* is more sensitive to oxidation than *apo*morphine itself; it has been obtained as a colourless, amorphous mass, which turns violet-coloured on exposure to the air.

Morphinequinnitrole nitrate, $C_{17}H_{18}O_6N_2,HNO_3,H_2O$, crystallises in brilliant, glistening, orange-yellow prisms when an excess of nitrous fumes is passed into an aqueous suspension of morphine. It cannot be recrystallised, and when its concentrated aqueous solution is warmed, morphinic acid (33%) is obtained, together with dark red, amorphous by-products. *Morphinic acid nitrate*, $C_{17}H_{19}O_6N,HNO_3,H_2O$, crystallises from hot water in colourless prisms, which turn brown on exposure to light. It has no definite melting point, does not give a coloration with ferric chloride, but reduces hot Fehling's solution. *Morphinic acid*, obtained by decomposing the nitrate with concentrated sodium acetate solution, is characterised by the deep green colour which it gives when warmed with water, and this, with a few drops of hydrochloric acid, changes to a cherry-red.

The *hydrochloride*, $C_{17}H_{19}O_6N,HCl,2H_2O$, crystallises in colourless needles.

Chloromorphide, prepared by the action of thionyl chloride on morphine, reacts with diethylamine at 100°, yielding *diethylaminomorphide*, $C_{21}H_{28}O_2N_2$, which crystallises from absolute alcohol in colourless prisms, m. p. 203°. The base is soluble in strong alkalis, but not in ammonia solution. The *hydrochloride* has m. p. 268° (decomp.), and gives a blue coloration with ferric chloride. The *methiodide*, $C_{22}H_{31}O_2N_2I$, has m. p. 268° (decomp.).

Dichlorodiacetylmorphine, $C_{21}H_{21}O_5NCl_2$, obtained by the action of chloroacetyl chloride on anhydrous morphine, crystallises from ether, has m. p. 135°, and readily loses one chloroacetyl group, yielding *chloroacetylmorphine*, $C_{19}H_{20}O_4NCl$, which crystallises from alcohol in colourless needles, m. p. 234° (decomp.).

Benzenesulphonylmorphine benzenesulphonate,

$$C_{23}H_{23}O_5NS,C_6H_5\cdot SO_3H,$$

crystallises from hot water in slender needles, m. p. 140°. The *base* has m. p. 165°. J. J. S.

Strychnine Alkaloids. XI. The Brucine–Nitric Acid Reaction. Preparation of a New Alkaloid, Bis*apo*methylbrucine. HERMANN LEUCHS and RUDOLPH ANDERSON (*Ber.*, 1911, 44, 2136—2145).—The colour reaction with nitric acid is shown, not only by brucine itself, but also by almost all its known derivatives and degradation products; in two instances, brucinesulphonic acid and brucinolone, substances have been isolated which behave like quinones, in that they can be reduced to the corresponding quinols. The present paper deals with the quinone and quinol corresponding with brucine itself.

Brucine is digested at 0° with 5*N*-nitric acid for half an hour, the red solution is reduced by sulphurous acid at 0°, and the quinol, *bis*apo*methylbrucine*, $C_{21}H_{22}O_4N_2$, prisms darkening at 260° and decomp. 285°, is purified by means of the *hydrochloride*, $C_{21}H_{22}O_4N_2,HCl$. The base develops an indigo-blue coloration with ferric chloride, reduces silver nitrate, and is readily soluble in alkalis.

By treating the red solution of brucine in nitric acid with an excess of cold saturated potassium hydrogen carbonate, a red *substance*, $C_{21}H_{21}O_6N_3$, is obtained, which is converted by chloroform and petroleum into the hydrated *quinone*, $C_{21}H_{20}O_4N_2,H_2O$, dark red needles, from which only one-half of the water can be expelled by intense drying. The anhydrous *quinone*, $C_{21}H_{20}O_4N_2$, red needles, is obtained by oxidising bis*apo*methylbrucine with chromic and sulphuric acids, whereby a red, crystalline *substance*, $C_{21}H_{20}O_4N_2,H_2CrO_4,HCl$, isolated by means of 5*N*-hydrochloric acid, is first obtained, which is converted into the anhydrous quinone by aqueous sodium hydrogen carbonate. After having once been isolated, the quinone and also its hydrate are not readily reduced to bis*apo*methylbrucine. C. S.

The Pyridine Compounds of the Tin Halides. PAUL PFEIFFER [with B. FRIEDMANN, R. LEHNARDT, H. LUFTENSTEINER, RUDOLF PRADE, and K. SCHNURMANN] (*Zeitsch. anorg. Chem.*, 1911, 71, 97—120. Compare Abstr., 1910, i, 852).—Tin forms four series of pyridine

compounds: SnX_4Py_2, $SnRX_3Py_2$, $SnR_2X_2Py_2$, and SnR_3XPy_2, giving, as before, the co-ordination number six, and confirming the constitutional formulæ previously given for the alkylated and phenylated compounds. Only the diphenylated stannic halides yield in addition additive compounds containing more than 2 mols. of pyridine. The iodides are also exceptional, the quantity of pyridine added depending on the number of iodine atoms. The difference is due to the additive power of the iodine atom.

Dipyridine tin tetrabromide, $SnBr_4Py_2$, prepared by adding dry pyridine to well cooled tin tetrabromide, is a white powder. Tin tetraiodide yields an unstable *compound*, $SnI_4Py_2,3Py$. *Dipyridine tin methyl trichloride*, $SnMeCl_3Py_2$, prepared from an ethereal solution of tin methyl chloride, and the *tribromide*, $SnMeBr_3Py_2$, are also amorphous. The tri-iodide yields a yellow additive *compound*, $SnMeI_3Py_2,2Py$. The following compounds have also been prepared: *dipyridine tin dimethyl dichloride*, $SnMe_2Cl_2Py_2$, colourless crystals, m. p. 163° (decomp.); the *dibromide*, $SnMe_2Br_2Py_2$, m. p. 172° (decomp.), and the *di-iodide*, $SnMe_2I_2Py_2$, m. p. 147° (decomp.).

Dipyridine tin dipropyl dichloride, $SnPr_2Cl_2Py_2$, forms colourless, glistening needles, m. p. 114°; the *dibromide* has m. p. 128°. *Dipyridine tin dibutyl dichloride*, $Sn(C_4H_9)_2Cl_2Py_2$, has m. p. 65—66°, and the *dibromide*, m. p. 77—78°.

Dipyridine tin diphenyl dichloride, $SnPh_2Cl_2Py_2$, is stable in air and has m. p. 151°. It also forms an additive *compound* with 2 mols. of pyridine, m. p. 155—156° (decomp.). The *dibromide*, $SnPh_2Br_2Py_2$, forms large crystals, m. p. 155° (decomp.), and also yields an additive *compound*, m. p. 160° (decomp.), with 2 mols. of pyridine. *Dipyridine tin ditolyl dibromide*, $Sn(C_6H_4Me)_2Br_2Py_2$, has m. p. 172—176°; *dipyridine tin triphenyl chloride*, $SnPh_3ClPy_2$, has m. p. 81—84°, and the *bromide*, m. p. 78—84°. C. H. D.

Preparation and Fission of Dihydroindole. JULIUS VON BRAUN and WLADISLAUS SOBECKI (*Ber.*, 1911, **44**, 2158—2161).—Dihydroindole, obtained from indole by Carrasco's electrolytic method, forms a *benzenesulphonyl* derivative, fine needles, m. p. 133°, and a *benzoyl* derivative, m. p. 118°. The latter is converted by phosphorus pentachloride in the usual manner into o-*β-chloroethylbenzanilide*, $CH_2Cl{\cdot}CH_2{\cdot}C_6H_4{\cdot}NHBz$, m. p. 120°, in 30% yield. C. S.

Preparation of β-Iodoindole. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, **73**, 128—130. Compare Abstr., 1909, i, 512).—2-Iodoindole can be prepared by the action of a solution of iodine in potassium iodide on a solution of indole and potassium hydroxide in water, and just sufficient alcohol to keep the compound in solution. It forms snow-white crystals, m. p. 72°, and turns black on exposure to the air. Scatole (2-methylindole) and tryptophan cannot be converted into iodo-derivatives by either method. J. J. S.

Dihydroquinaldine Bases. GUSTAV HELLER [with SIEGMUND SCHMEJA] (*Ber.*, 1911, **44**, 2106—2115).—It has been shown previously (Heller and Sourlis, Abstr., 1908, i, 914) that 2-methyl-

quinoline, when heated with zinc dust and hydrochloric acid, yields 2-methyldihydroquinoline. This method of reduction has now been applied to the preparation of the dihydro-derivatives of several isomeric methylquinolines and dimethylquinolines. These dihydro-bases are all bimolecular, and cannot be further reduced to the corresponding tetrahydro-compounds. From their indifference towards methyl iodide, and the fact that they yield neither nitrosoamines nor acetyl derivatives, the authors draw the conclusion that the nitrogen atom in these compounds is no longer tervalent. When heated with mercuric oxide in cumene solution or with chromium trioxide in glacial acetic acid solution, the dihydro-bases are oxidised to the corresponding quinolines.

2-*Methyldihydroquinoline hydrochloride*, $C_{10}H_{11}N,HCl$, crystallises in lustrous needles, which become brown at 210°, and have m. p. 250°; the *sulphate*, $2C_{10}H_{11}N,H_2SO_4$, crystallising in lustrous leaflets, becomes brown at 210°, and decomposes at 240°.

2-Methyldihydroquinoline condenses with chloral hydrate, formaldehyde, and phthalic anhydride, but the products thus formed could not be obtained crystalline. When treated with bromine in chloroform solution, it yields *dibromo-2-methyldihydroquinoline*, $C_{10}H_9NBr_2$. This crystallises in lustrous, colourless needles, m. p. 242° (decomp.), and is not oxidised by mercuric oxide. Its stability towards alcoholic potassium hydroxide and reducing agents indicates that the bromine atoms have probably entered the benzene nucleus. Unsuccessful attempts have been made to synthesise the dihydro-compound from *o*-nitrostyryl methyl ketone (Baeyer and Drewsen, Abstr., 1883, 341). The latter compound, when treated with bromine in glacial acetic acid solution, yields the *dibromide*, $NO_2{\cdot}C_6H_4{\cdot}CHBr{\cdot}CHBr{\cdot}COMe$, which crystallises in colourless needles, m. p. 102°, and is reduced by zinc and acetic acid to 2-methylquinoline and 2-methyltetrahydroquinoline.

2 : 8-*Dimethyldihydroquinoline* crystallises in colourless needles, m. p. 216—217°, and has no basic properties. When treated with bromine in hot alcoholic or glacial acetic acid solution it yields a *tetrabromo*-derivative, $C_{11}H_9NBr_4$ (?), which forms sulphur-yellow crystals, m. p. 171—172°. Bromination in dilute alcoholic solution results in the formation of a *tribromo*-derivative, $C_{11}H_{10}NBr_3$, m. p. 121—122°, whilst in chloroform or benzene solution the action of bromine yields a *substance*, m. p. 240—250°, containing only two atoms of bromine in the molecule.

2 : 6-*Dimethyldihydroquinoline* has m. p. 143°; the *hydrochloride* forms white needles, which become brown at 205°, and have no definite m. p.; the *hydrobromide*, crystallising in lustrous needles, becomes brown at 215°, and has m. p. 260°; the *sulphate*,

$$2C_{11}H_{13}N,H_2SO_4,$$

has m. p. 220° (decomp.), becoming brown at 206°.

The behaviour of 2 : 6-*dimethyldihydroquinoline* towards bromine resembles that of the isomeric 2 : 8-compound; the *tetrabromo*-derivative, $C_{11}H_9NBr_4$, obtained by bromination in hot glacial acetic acid solution, crystallises in pale yellow needles, m. p. 172°.

2 : 7-*Dimethyldihydroquinoline* is amorphous, and on account of its feebly basic properties could not be further purified.

The reduction of quinoline by zinc and hydrochloric acid takes place at the ordinary temperature, dihydroquinoline together with a small quantity of tetrahydroquinoline being produced.

8-*Methyldihydroquinoline*, $C_{10}H_{11}N$, has m. p. 144°; the *hydrochloride*, m. p. 278°.

6-*Methyldihydroquinoline* melts indefinitely at 60—105°, forms no salts, and therefore could not be further purified.

By distilling dihydroglauconic acid or by heating 2-methylquinoline hydrochloride with zinc dust, Doebner (Abstr., 1898, i, 384) obtained a substance which he considered to be 2-methyldihydroquinoline. According to the author this consists of 2-methylquinoline, whilst Doebner's dihydro-2 : 6-dimethylquinoline (Abstr., 1900, i, 313) is identical with 2 : 6-dimethylquinoline. F. B.

Cyanodihydrocyclic Amines. IV. Synthesis of Cinchonic Acid. ADOLF KAUFMANN and ROBERT WIDMER [with ALBERTO ALBERTINI] (*Ber.*, 1911, 44, 2058—2065).—On oxidation of 4-cyano-1-methyldihydroquinoline, $C_6H_4<\begin{matrix}CH(CN)\cdot CH\\ NMe——CH\end{matrix}$, with alcoholic iodine solution, it is readily converted into the methiodide of 4-cyanoquinoline, $C_6H_4<\begin{matrix}C(CN):CH\\ NMeI:CH\end{matrix}$, which, on hydrolysis, forms the methiodide of cinchonic acid, $C_6H_4<\begin{matrix}C(CO_2H):CH\\ NMeI==CH\end{matrix}$. Both iodides are oxidised by alkaline ferric cyanide solution to known α-quinolones, and the betaine of 1-methylcinchonic acid is obtained on treating the methiodide with moist silver oxide.

4-Cyanoquinoline is conveniently prepared by heating 4-cyanoquinoline methiodide in a stream of carbon dioxide at 210—220°, when methyl iodide is eliminated, and the nitrile sublimes in long, colourless needles, m. p. 95°.

In general, cyclaminones when distilled with zinc dust form cyclamine bases; thus, 4-cyano-1-methyl-2-quinolone yields the nitrile of cinchonic acid.

Cyanodihydroacridines are unaffected by alcoholic iodine solution, and the cyano-group cannot be displaced by bromine, which, however, forms a dibromo-derivative, *dibromocyanophenylmethyldihydroacridine*, crystallising in colourless, cubic crystals, m. p. 208—209°. From analogy to the experiments of Dunstan and Oakley (Abstr., 1906, i, 383), the bromine atoms are considered to occupy the 3 : 6-positions.

4-*Cyanoquinoline methiodide* forms red needles, which darken at 180°, m. p. 216° (decomp.).

On bromination of phenylmethyldihydroacridone, the *methobromide* of *dibromophenylacridine* is obtained in orange-yellow needles, m. p. 274° (decomp.). Potassium cyanide converts it into the dibromocyanophenylmethyldihydroacridine just described. With alcoholic potassium hydroxide, a reddish-violet coloration is obtained, and yellow needles separate of the *ethyl ether* of 3 : 7-*dibromo-5-phenyl-10-methyldihydroacridinol*; they become violet at 170°, m. p. 192—195°

(decomp.). 3 : 7-*Dibromo*-5-*cyano*-5 : 10-*dimethyldihydroacridine* forms strongly refractive cubes, which blacken at 220°, m. p. 228°. E. F. A.

Formation of *iso*Quinoline Derivatives by the Action of Methylal on Phenylethylamine, Phenylalanine, and Tyrosine. AMÉ PICTET and THEODOR SPENGLER (*Ber.*, 1911, **44**, 2030—2036).—Tetrahydro*iso*quinoline derivatives are obtained directly on condensing substituted phenylethylamines with aldehydes instead of with acids, as in the Bischler-Napieralski synthesis, which leads to unsaturated *iso*quinolines. Thus from formaldehyde and β-phenylethylamine, tetrahydro*iso*quinoline is obtained without difficulty, and the reaction gives still better results with phenylalanine and tyrosine, which yield with formaldehyde, tetrahydro- and hydroxytetrahydro-*iso*quinolinecarboxylic acids.

In view of the fact that all these substances are natural plant products, it is very probable that a similar condensation takes place in the plant, and that the relatively simple tetrahydro*iso*quinoline compounds formed after loss of the carboxyl group become methylated and undergo further complication until the various *iso*quinoline alkaloids are obtained. The latter may now be regarded as modified degradation products of vegetable protein. Such alkaloids as laudanosine represent a primary condensation of amino-acid and formaldehyde, and a secondary condensation of this product with a substituted benzaldehyde.

*Tetrahydro*iso*quinoline-3-carboxylic acid*, $C_6H_4<\begin{matrix}CH_2\cdot CH\cdot CO_2H \\ CH_2\cdot NH\end{matrix}$, prepared from phenylalanine and methylal, crystallises in large, nacreous, colourless plates, m. p. 311° (decomp.). On heating above the melting point, tetrahydro*iso*quinoline is formed.

7-*Hydroxytetrahydro*iso*quinoline-3-carboxylic acid*,

$$OH\cdot C_6H_3<\begin{matrix}CH_2\cdot CH\cdot CO_2H \\ CH_2\cdot NH\end{matrix},$$

forms a colourless, microcrystalline precipitate, m. p. 336—338° (decomp.). When heated, a secondary base, probably 7-*hydroxytetrahydro*iso*quinoline* is obtained, b. p. 210—220°/18 mm.; the *picrate* has m. p. 198—201°. The *hydrochloride*, when distilled with zinc dust, gives *iso*quinoline. E. F. A.

Cyanodihydrocyclic Amines. III. ADOLF KAUFMANN and ALBERTO ALBERTINI [with ROBERT WIDMER] (*Ber.*, 1911, **44**, 2052—2058. Compare Abstr., 1909, i, 606, 958).—5-Cyano-5-phenyldihydroacridine, probably on account of steric hindrance, could not be converted into the corresponding acid, and, similarly, 5-cyano-10-methyldihydroacridine, on account of the readiness of its oxidation to 10-methylacridone, could not be hydrolysed.

5-Cyano-5 : 10-dimethyldihydroacridine, $CN\cdot CMe<\begin{matrix}C_6H_4 \\ C_6H_4\end{matrix}>NMe$, however, yields a carboxylic acid, from which carbon dioxide is eliminated on recrystallisation, and the corresponding dihydroacridine, $CHMe<\begin{matrix}C_6H_4 \\ C_6H_4\end{matrix}>NMe$, obtained.

10-*Methylacridine tartrate* crystallises in green needles of silky lustre, m. p. 153—154° (decomp.). The picrate crystallises with a molecule of alcohol in greenish-yellow needles, m. p. 213—214° (Decker gives 220—221°). The *mercurichloride* forms yellow needles, m. p. 258°; the methiodide golden, glistening platelets, decomp. 200°, m. p. 235—245° (Bernthsen, 185°); the *methochloride* separates in glistening, yellow platelets, m. p. 200°, and gives a yellow crystalline precipitate, m. p. 252—255°, with platinum chloride and brown needles, m. p. 193—194° (explosively), with picric acid.

5-*Cyano*-5 : 10-*dimethyldihydroacridine*, formed by the interaction of methylacridine methochloride and potassium cyanide, separates in colourless crystals, m. p. 123°. The *picrate* crystallises in dark brown plates, m. p. 138—139°.

5-*Cyano*-10-*methyl*-5-*benzyldihydroacridine* crystallises in colourless needles, m. p. 125°.

5 : 10-*Dimethyldihydroacridine*-5-*carboxylic acid*, prepared by hydrolysis of the cyano-compound with alcoholic potassium hydroxide, crystallises in colourless, glistening plates, which blacken at 130°, m. p. 160° (decomp.). Carbon dioxide is readily eliminated, and 5 : 10-dimethyldihydroacridine obtained in lanceolate, yellow crystals, m. p. 137° (compare Freund and Bode, Abstr., 1909, i, 514).

E. F. A.

Action of Hydrazine on Carbonyl Compounds. Hermann Staudinger and Otto Kupfer (*Ber.*, 1911, **44**, 2197—2212).—Curtius and his co-workers found that the products obtained from hydrazine and ordinary aldehydes or ketones differed greatly in behaviour from those produced by the interaction of hydrazine and benzil or α-ketonic esters; the former class, therefore, were regarded as hydrazones, $>C:N\cdot NH_2$, and the latter as derivatives of hydrazimethylene, $>C<{NH \atop NH}$. The authors now show that the members of both classes all behave alike under suitable conditions, and are therefore constituted alike, although they are unable to state whether the substances are hydrazones or hydrazimethylenes. One of the chief criteria of members of the second class is their oxidation to azomethylenes, $>C<{N \atop N}$, by mercuric oxide. However, the hydrazones of fluorenone, dimethoxybenzophenone (*dimethoxybenzophenonehydrazone* has m. p. 84—86°), benzophenone, and acetophenone also yield azomethylene derivatives, which decompose in various ways according to their varying stability; these decompositions are initially the formation of nitrogen and the group $RR'C<$, which, by intramolecular change, polymerisation, or interaction with undecomposed azomethylene, may yield non-nitrogenous or nitrogenous compounds. The action of iodine on these azomethylene derivatives also starts with the formation of nitrogen and the group $RR'C<$, which then undergoes change as above or unites with iodine to form substituted methylene iodides.

Diphenyleneazomethylene, ${C_6H_4 \atop C_6H_4}>C<{N \atop N}$, m. p. 94—95°, dark red

needles, is unimolecular (so also are all other azomethylene derivatives); it yields bisdiphenylene-ethylene when decomposed by heat at 130—140° (in the presence of a little benzene or ether), by iodine in boiling alcohol, or by hydrogen bromide in boiling xylene, and is reduced to fluorene by zinc and alcoholic sodium hydroxide. *Dimethoxydiphenylazomethylene*, $\overset{N}{\underset{N}{|\,|}}\!\!>C(C_6H_4{\cdot}OMe)_2$, m. p. 103—104°, deep violet crystals, changes in air or in hot benzene to the ketazine, yields tetramethoxytetraphenylethylene when heated with benzene at 150° in an atmosphere of carbon dioxide, and is converted into dimethoxybenzophenone when shaken in benzene in an atmosphere of oxygen. Diphenylazomethylene is converted completely into the ketazine by heat at 150°.

The formation of azomethylenes by the oxidation of the products of the interaction of hydrazine and carbonyl compounds would suggest that these products are hydrazimethylenes. However, against this assumption and in favour of the hydrazone formula are the facts: (i) the azomethylenes cannot be re-converted into hydrazimethylenes by reduction; (ii) the behaviour of the products is easily explained by the hydrazone formula; (iii) almost all of the products are very easily converted into ketazines; (iv) the acetylation of benzylidenehydrazine yields a substance identical with that obtained from acetylhydrazine and benzaldehyde. All hydrazones behave alike when heated, primarily yielding ketazines and hydrazine, by the further interaction of which methane derivatives may be formed; thus the hydrazone of benzil, which gives deoxybenzoin when heated under Curtius's conditions, is converted into bisbenzilketazine at 240°/11 mm. Similarly, fluorenonehydrazone at 200°/18 mm. yields the ketazine (which is converted into fluorene by an excess of hydrazine hydrate at 200°), and dimethoxybenzophenonehydrazone yields bisdimethoxydiphenylketazine at 280°/20 mm., which is converted into dimethoxydiphenylmethane by an excess of hydrazine at 200°. The hydrazone of Michler's ketone yields the ketazine at 280°/14 mm., which is reduced to tetramethyldiaminodiphenylmethane by an excess of hydrazine at 200°. Benzophenone, benzophenoneanil, and benzophenonephenylhydrazone are reduced to diphenylmethane, and benzylideneazine and benzaldehyde to toluene, by an excess of hydrazine at 200°. C. S.

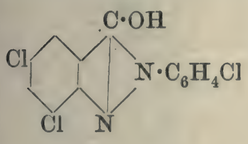
Synthesis of Iminazole [Glyoxaline] Derivatives. ADOLF WINDAUS and H. OPITZ (*Ber.*, 1911, 44, 1721—1725. Compare Windaus and Vogt, Abstr., 1907, i, 978).—4-*Aminomethylglyoxaline*, $\begin{matrix}CH{=\!=}N\\ |\\ NH{\cdot}CH\end{matrix}\!\!>C{\cdot}CH_2{\cdot}NH_2$, is obtained from glyoxaline-4-acetic acid (Knoop, Abstr., 1907, i, 789) by Curtius' method. The *hydrazide*, $C_5H_8ON_4$, prepared by boiling ethyl glyoxaline-4-acetate for six hours with a 50% hydrazine hydrate solution, crystallises from absolute alcohol in needles, m. p. 189° (decomp.). The *dihydrochloride* crystallises in prisms insoluble in alcohol, has m. p. 230°, and with amyl nitrite and alcohol yields the urethane, and this when hydrolysed with

concentrated hydrochloric acid gives 4-*aminomethylglyoxaline hydrochloride*, which crystallises from a mixture of methyl alcohol and ether in long, slender prisms, sintering at 236°.

The *platinichloride*, $C_4H_9N_3Cl_6Pt$, crystallises in compact, rhombic plates, which decompose at 288°; the *picrate* crystallises from hot water in deep yellow, glistening, six-sided plates, m. p. 209°, and the *picrolonate*, $C_{24}H_{23}O_{10}N_{11}$, forms long, yellow needles, m. p. 273° (decomp.).

4-*β-Hydroxyethylglyoxaline*, $\begin{matrix}CH{=}N\\ | \\ NH{\cdot}CH\end{matrix}{>}C{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ (?), is obtained by the action of barium nitrite on 4-*β*-aminoethylglyoxaline hydrochloride, and is probably identical with the product formed by the action of yeast on histidine (Ehrlich, this vol., i, 127). The *hydrochloride* crystallises from water in nodular masses of needles; the *platinichloride* forms orange-yellow needles, m. p. 175°, and the *picrolonate* crystallises from alcohol in slender, pale yellow needles, which are much bent, and have m. p. 264° (decomp.). When the hydroxy-compound is treated with 25% nitric acid, the chief product is 5-*nitroglyoxaline*-4-*carboxylic acid*, $\begin{matrix}CH{=\!=}N\\ | \\ NH{\cdot}C(NO_2)\end{matrix}{>}C{\cdot}CO_2H$, which crystallises from water in long, colourless prisms, m. p. above 300° (decomp.). J. J. S.

Hydroxyindazoles. IV. Preparation of Hydroxyindazoles from Non-substituted Benzene-azo- or -hydrazo-benzoic Acids. PAUL FREUNDLER (*Bull. Soc. chim.*, 1911, [iv], 9, 735—739. Compare Abstr., 1903, i, 371, 585; 1904, i, 121, 667, 699; 1906, i, 544; this vol., i, 577).—The method described gives a ready means for preparing unchlorinated or mono-chlorinated hydroxyindazoles, which up to the present have been difficult to obtain. The transformation consists in a simple dehydration, and proceeds more readily when there are more halogen atoms in the benzene nucleus.



5 : 7-*Dichloro*-3-*hydroxy*-2-p-*chlorophenylindazole* (annexed formula), white needles, m. p. 209—210°, very sparingly soluble in organic solvents, is prepared by the action of phosphorus pentachloride or thionyl chloride on *p*-chlorobenzeneazo-*o*-benzoic acid.

The same method is used for the preparation of several hydroxyindazoles, which have been previously prepared by other methods, and described. 5 : 7-Dichloro-3-hydroxy-2-phenylindazole can be readily obtained from benzeneazo-*o*-benzoic acid in this way (compare Abstr., 1907, i, 158). W. G.

Ring Formation in the Peri-position in the Naphthalene Series. III. Derivatives of 2′ : 4′-Dinitrophenyl-1 : 8-naphthylenediamine. FRANZ SACHS and R. B. FORSTER (*Ber.*, 1911, 44, 1738—1748. Compare Abstr., 1909, i, 426).—The condensation of 2′ : 4′-dinitrophenyl-1 : 8-naphthylenediamine with various acids and carbonyl derivatives has been studied. In the case of

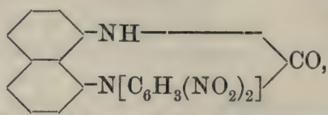
condensing with formic acid, the large, strongly negative dinitrophenyl group has a retarding effect. With acetic anhydride and most acyl chlorides, ring formation does not occur, the product being a monoacyl derivative of the type

$$R\cdot CO\cdot NH\cdot C_{10}H_6\cdot NH\cdot C_6H_3(NO_2)_2.$$

Carbonyl chloride does not condense at all readily with the nitrated base, but ethyl chlorocarbonate yields the *carbethoxy*-derivative,

$$CO_2Et\cdot NH\cdot C_{10}H_6\cdot NH\cdot C_6H_3(NO_2)_2,$$

which gives the cyclic compound 1-*op*-dinitrophenyl-1 : 3-dihydro-2-perimidone :

(I.) 

Ethyl oxalate yields a mixture of the two compounds

$$\text{(II.)}\ CO_2Et\cdot CO\cdot NH\cdot C_{10}H_6\cdot NH\cdot C_6H_3(NO_2)_2$$

and (III.) $\begin{array}{l} N{=\!=\!=}C\cdot CO_2Et \\ | \qquad\ \ | \\ C_{10}H_6\cdot N\cdot C_6H_3(NO_2)_2 \end{array}$, and succinic anhydride reacts in much the same manner.

Condensation with phthalic anhydride takes place readily when a glacial acetic acid solution of the components is boiled for a short time, the product being 1-*op*-dinitrophenylperimidine-2-benzoic acid,

$$\begin{array}{l} N{=\!=\!=}C\cdot C_6H_4\cdot CO_2H \\ | \qquad\ \ | \\ C_{10}H_6\cdot N\cdot C_6H_3(NO_2)_2 \end{array}.$$

Acetone, ethyl acetoacetate, and other carbonyl derivatives react with the free amino-group only, ring formation does not occur, and products of the type (IV.) $C_6H_3(NO_2)_2\cdot NH\cdot C_{10}H_6\cdot N\!:\!CMe_2$ are formed, which are extremely sensitive to acids.

The cyclic perimidine compounds obtained are deeply coloured; their solutions in concentrated sulphuric acid are also coloured, and the colour of the solution is not destroyed by gently heating.

1-op-*Dinitrophenylperimidine*, $\begin{array}{l} N{=\!=\!=}CH \\ | \qquad\ \ | \\ C_{10}H_{16}\cdot N\cdot C_6H_3(NO_2)_2 \end{array}$, crystallises from dilute methyl alcohol in reddish-brown needles, m. p. 175°, and decomposing at 265°. The *picrate*, $C_{23}H_{13}O_{11}N_7$, forms orange-red crystals, m. p. 232°.

1-*Acetylamino*-8-op-*dinitroanilinonaphthalene*,

$$NHAc\cdot C_{10}H_6\cdot NH\cdot C_6H_3(NO_2)_2,$$

separates from alcohol in yellow crystals, m. p. 237°, and yields a *tetranitro*-derivative, m. p. 248°. The corresponding *benzoyl* derivative, $COPh\cdot NH\cdot C_{10}H_6\cdot NH\cdot C_6H_3(NO_2)_2$, crystallises from glacial acetic acid or xylene, and has m. p. 271—272°, and the *cinnamoyl* derivative, $CHPh\!:\!CH\cdot CO\cdot NH\cdot C_{10}H_6\cdot NH\cdot C_6H_3(NO_2)_2$, separates in yellow crystals from xylene, and has m. p. 258—259°.

1-*Carbethoxylamino*-8-op-*dinitroanilinonaphthalene*,

$$CO_2Et\cdot NH\cdot C_{10}H_6\cdot NH\cdot C_6H_3(NO_2)_2,$$

obtained by heating the dinitrated base with ethyl chlorocarbonate at 100° for seventeen hours, forms orange-coloured crystals, m. p. 184—185°, and decomposing at 260—270°. When heated at 193° under 10—12 mm. pressure for $1\frac{1}{2}$ hours, the compound loses ethyl alcohol

and yields 1-op-*dinitrophenyl*-1 : 3-*dihydro*-2-*perimidone*, $C_{17}H_{10}O_5N_4$, which crystallises from xylene in red, triangular prisms, m. p. 267—268° (decomp.), after changing colour at 150°. The crystals contain 0·5 mol. of xylene, which they lose gradually at 100° under reduced pressure.

8-op-*Dinitroanilino*-1-*naphthylphenylcarbamide*,

$$C_6H_3(NO_2)_2\cdot NH\cdot C_{10}H_6\cdot NH\cdot CO\cdot NHPh,$$

obtained by heating the components in dry xylene, separates from acetic acid in orange-coloured crystals, m. p. 229—230°, and the corresponding *thiocarbamide*, $C_{23}H_{17}O_4N_5S$, obtained by boiling a chloroform solution of the components for twenty-four hours, separates from a mixture of chloroform and light petroleum in glistening, orange-red crystals, m. p. 182°.

Methyl 8-op-*dinitroanilinonaphthyloxamate*,

$$C_6H_3(NO_2)_2\cdot NH\cdot C_{10}H_6\cdot NH\cdot CO\cdot CO_2Me,$$

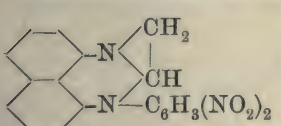
obtained by heating the dinitro-base with ten times its weight of methyl oxalate for seven days at 100°, crystallises from dilute acetone, and has m. p. 209—210°. The corresponding *ethyl* ester separates from ethyl acetate in yellow crystals, m. p. 191—192°, and is accompanied by the cyclic compound (III), which forms red crystals, m. p. 171—172°.

8-op-*Dinitroanilino*-1-*naphthylsuccinamic acid*,

$$C_6H_3(NO_2)_2\cdot NH\cdot C_{10}H_6\cdot NH\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H,$$

forms a pale yellow, crystalline powder, turns red at 190°, and decomposes at 227°. When boiled with glacial acetic acid it yields the *anhydro*-compound, $C_{20}H_{14}O_6N_4$, in the form of red crystals sparingly soluble in alcohol and melting at 227°.

1-op-*Dinitrophenylperimidine*-2-*benzoic acid* forms yellow crystals, m. p. 297°, and when reduced yields the corresponding *diamino*-derivative, which is not molten at 340°, although its *picrate* has m. p. 220°.



The dinitro-base reacts with formaldehyde solution in the presence of glacial acetic acid and dilute hydrochloric acid, yielding a compound, probably of the annexed constitution, which decomposes without melting.

8-op-*Dinitroanilino*-1-*propylideneamino*-*naphthalene* (IV), from acetone and the dinitro-base, forms yellow crystals, m. p. 166—167°. The corresponding *derivative* from acetophenone,

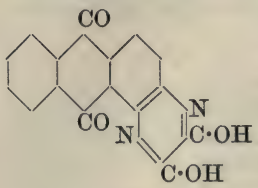
$$C_6H_3(NO_2)_2\cdot NH\cdot C_{10}H_6\cdot N\colon CMePh,$$

forms red crystals, m. p. 163—164°, and that from ethyl acetoacetate, $C_6H_3(NO_2)_2\cdot NH\cdot C_{10}H_6\cdot N\colon CMe\cdot CH_2\cdot CO_2Et$, has m. p. 167—168°.

J. J. S.

Degradation of Indanthren to Dihydroxypyrazinoanthraquinone and its Behaviour with Benzoyl Chloride and Sodium Ethoxide. ROLAND SCHOLL and SIEGFRIED EDLBACHER (*Ber.*, 1911, 44, 1727—1737. Compare Scholl and Mansfield, Abstr., 1907, i, 255).—Commercial indanthren powder which has been extracted with hydrochloric and glacial acetic acids can be oxidised by

a boiling glacial acetic acid solution of chromium trioxide to *αβ-dihydroxyanthraquinoxalinequinone* (*αβ-dihydroxy-1 : 2-pyrazinoanthraquinone*) (annexed constitution), which crystallises from nitrobenzene in golden-bronzy needles. It begins to sublime at 300°, and chars at 370°. Boiling sulphuric acid or bromine has no action, and distillation with zinc dust yields anthraquinoxaline. Its *sodium* derivative,



$C_{16}H_6O_4N_2Br_2$,

obtained by the action of sodium ethoxide, forms a brick-red powder.

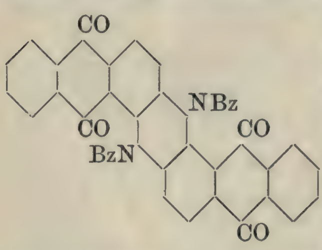
Nitrodihydroxyanthraquinoxalinequinone, $C_{16}H_7O_6N_3$, obtained by the action of 50% nitric acid, forms a pale yellow powder, and yields a red sodium derivative. The corresponding *amino*-derivative,

$C_{16}H_9O_4N_3$,

prepared by reducing the nitro-compound with ammonium sulphide, crystallises from nitrobenzene in violet, microscopic needles, m. p. 365°.

αβ-Dihydroxyanthraquinoxalinequinone can be synthesised by condensing 1 : 2-diaminoanthraquinone with anhydrous oxalic acid at 170°.

Indanthren yields *N*-benzoyl derivatives (compare Scholl and Berblinger, Abstr., 1907, i, 257) when boiled for an hour with benzoyl chloride or benzoic anhydride. The *dibenzoyl* derivative, *dibenzoyl-N-dihydroanthraquinoneazine* (annexed constitution), crystallises from xylene in red needles, forms an unstable blue additive compound with benzoyl chloride, and is hydrolysed by sulphuric acid or by alcoholic potash to indanthren.



When indanthren is left in contact with a methyl-alcoholic solution of sodium methoxide at the ordinary temperature for twenty-four hours, the colour changes to greyish-green, and, after decanting and washing with methyl alcohol and ether, and finally with absolute ether, a bluish-black sodium compound is obtained. This product is formed by the union of two molecules of sodium methoxide to one of the quinone, probably at the expense of two of the four carbonyl groups originally present. The compound is immediately decomposed by water.

Anthraquinoneazine and sodium methoxide form a green additive compound, $C_{30}H_{18}O_6N_2Na_2$, which is completely decomposed by prolonged treatment with methyl alcohol, yielding anthraquinonazhydrine (Abstr., 1904, i, 110). These compounds are analogous to the additive compounds of sodium alkyl oxides with indigocarmine, indigotin, etc.

J. J. S.

Constitution of Alloxantin. M. M. Richter (*Ber.*, 1911, 44, 2155—2158).—Piloty and Finckh, and also Slimmer and Stieglitz, have suggested that alloxantin is a combination of alloxan and

dialuric acid resembling the quinhydrones. Since alloxantin does not exhibit the typical criteria (quinonoid structure, colour, easy dissociation) of quinhydrones, the proof of the suggestion is very difficult, and must be limited to the possibility of preparing quinhydrone-like compounds from *p*-benzoquinone and dialuric acid and from quinol and alloxan. The combination of the former pair is impossible, owing to the sensitiveness of dialuric acid to atmospheric oxidation, but a molecular combination of the latter pair has been described by Böhringer & Söhne (1900, D.R.-P. 107720). That the oxygen atom in alloxan can exert a similar, although milder, oxidising action to that of the oxygen in *p*-benzoquinone is shown by mixing concentrated aqueous solutions of alloxan and *p*-phenylenediamine at 30°, whereby is obtained a bluish-black precipitate of p-*phenylenedi-imine dialurate*, $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot O\cdot NH_2{:}C_6H_4{:}NH$, the formation of which is explained by the conversion of the *p*-phenylenediamine and the alloxan into *p*-phenylenedi-imine and dialuric acid respectively.

Alloxan and hydrazine hydrate in methyl alcohol yield *alloxan-hydrazine*, $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C{:}OH\cdot NH\cdot NH_2$ (according to the author's oxonium formula for quinhydrones), a white, amorphous powder, which in the presence of moisture is transformed into *dialurodi-imine*, $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot O\cdot NH_2{:}NH$, decomposing rapidly into nitrogen and ammonium dialurate. C. S.

Benzeneazoxy-*o*-benzoic Acid. PAUL FREUNDLER (*Bull. Soc. chim.*, 1911, [iv], 9, 739—741).—*Benzeneazoxy-*o*-benzoic acid*, $O<\begin{matrix}N\cdot C_6H_4\cdot CO_2H\\ | \\NPh\end{matrix}$, pale yellow spangles, m. p. 110—111°, is prepared by the action of phenylhydroxylamine on *o*-nitrosobenzoic acid in alcoholic solution. It is purified through its barium salt. W. G.

Hydroxyindazoles. III. Preparation of Ortho-substituted Azo-acids. PAUL FREUNDLER (*Bull. Soc. chim.*, 1911, [iv], 9, 657—661. Compare this vol., i, 577).—Further condensations of nitrosobenzene with *o*-aminobenzoic esters and of amines with *o*-nitrosobenzoic acids have been effected by the method previously described.

Methyl 5-chloroanthranilate and nitrosobenzene when kept for fifteen days at the ordinary temperature in glacial acetic acid yield a reaction product, from which the following substances can be isolated: (1) the yellow compound, $C_{13}H_{11}O_3N_2Cl$, m. p. 137°, previously mentioned (Abstr., 1910, i, 446); (2) *methyl 2-benzeneazo-5-chlorobenzoate*, which forms red needles, m. p. 64·5°; (3) the *acid*, of which the yellow compound is the methyl ester; (4) azoxybenzene; (5) 2-*benzeneazo-5-chlorobenzoic acid*, which, after purification by the crystallisation of its *barium* salt, forms orange-red needles, m. p. 126—127°. The *barium* salt becomes red and anhydrous at 100°.

Methyl bromoanthranilate yields in similar circumstances: (1) a yellow *substance*; (2) the corresponding *acid*; (3) azoxybenzene; (4)

2-*benzeneazo-5-bromobenzoic acid*, which crystallises in ruby-red prisms, m. p. 142—143°.

By the interaction of *o*-nitrosobenzoic acid and aniline, benzeneazobenzoic acid is obtained, and *p*-tolueneazobenzoic acid and *p*-chlorobenzeneazobenzoic acid may be prepared similarly.

2-*Nitroso*-m-*toluic acid* crystallises in grey prisms, m. p. 172—173° (decomp.). It reacts with *p*-toluidine, yielding 2-p-*tolueneazo*-m-*toluic acid*, which crystallises in large, red prisms, m. p. 122·5°.

2-p-*Tolueneazo-5-chlorobenzoic acid* (from *p*-toluidine and 2-nitroso-5-chlorobenzoic acid) forms orange scales, m. p. 159—160°.

R. V. S.

Sulphur Linkings in Proteins. Treat B. Johnson (*J. Biol. Chem.*, 1911, 9, 439—448).—The available evidence on the sulphur linkings in protein is summarised and discussed. It is considered that there are other sulphur combinations besides the cystine group which can break down on hydrolysis with the formation of hydrogen sulphide. E. F. A.

Enzyme Action and Electrolytic Dissociation. Hugo Rohonyi (*Biochem. Zeitsch.*, 1911, 34, 176—191).—The differences which have been observed between active and inactivated enzyme solutions are experimentally shown by the author to be due to the evaporation of water during the process of inactivation. The increase in conductivity during the course of the hydrolysis of starch by diastase is shown to be due to the setting free of adsorbed salt molecules. No similar increase is observed when ash-free sucrose is hydrolysed by invertin. On the addition of a substrate to an enzyme solution the changes of the conductivity are quantitatively different when active or inactivated enzyme is used. This change is not specific for the substrate, however, as similar differences are noted when indifferent electrolytes are added to the enzyme solutions. The hydrogen ion concentration in the cases investigated remains unchanged during the digestion process, and there is no difference in the hydrogen ion concentration between active and inactivated enzyme solutions. S. B. S.

Action of Ultra-violet Light on Amylase, Invertase, and a Mixture of These Two Diastases. A. Chauchard and (Mlle.) B. Mazoué (*Compt. rend.*, 1911, 152, 1709—1711).—Malt amylase is much more sensitive to ultra-violet light than the invertase from yeast. It is therefore possible by exposing a mixture of the two to the light from a quartz-mercury lamp to destroy the activity of one before that of the other. W. O. W.

The Solubility of the Pancreas Lipase. L. Berczeller (*Biochem Zeitsch.*, 1911, 34, 170—175).—Experiments with pancreas lipase showed that this enzyme is not soluble either in ether, fats, or fatty acids. The conclusion is drawn that the fat scission by lipase takes place in a heterogeneous system. S. B. S.

Enzymic Decomposition of Hydrogen Peroxide. PERCY WAENTIG and OTTO STECHE (*Zeitsch. physiol. Chem.*, 1911, **72**, 226—304. Compare Senter, Abstr., 1905, i, 107; ii, 377).—The decomposition of hydrogen peroxide by the enzymes of blood is not in agreement with a reaction of the first order, nor is it possible to express the course of change by one mathematical expression. There is, however, some proportionality between the enzyme concentration and the amount of hydrogen peroxide decomposed during the first stage of the reaction.

The more highly purified ferment preparations are more susceptible to the adverse influence of impurities. Hydrogen peroxide exerts an adverse influence.

The neutrality or otherwise of the mixture is of great influence on the velocity of reaction, which is quickest at 0° in truly neutral distilled water, and is retarded by the amount of carbon dioxide present in ordinary distilled water or by addition of alkali until indicated by phenolphthalein. At higher temperatures the optimum is in water containing carbon dioxide. When the quantity of acid present is increased, the velocity of change falls at first quickly and later more slowly without the enzyme being damaged. An increase in the amount of alkali decreases the velocity, and the enzyme is also in part destroyed. These changes are more marked at 30° than at 0°.

The influence of an increase of temperature on the rate of change is remarkably small so long as the concentration of the hydrogen peroxide is small. E. F. A.

The Reducing Ferments. II. Reduction of Nitrates by the System Perhydrase, Aldehyde, Water. ALEXIS BACH (*Biochem. Zeitsch.*, 1911, **33**, 282—290).—The author has already suggested that the Schardinger enzyme which reduces methylene-blue is a perhydrase which acts together with another substance which can be replaced by aldehydes (this vol., i, 412). The reducing action when methylene-blue is replaced by nitrates was then investigated. It was found that fresh milk contains a catalase, which accelerates the reduction of nitrates by aldehydes to such an extent that nitrites could be detected after one or two minutes' action. The increase of both aldehyde and nitrate concentration increases the rate of action, but the increased rate is less than proportional to the increase of the other two constituents of the system. The increased rate of action is, however, proportional to the concentration of the enzyme when the concentration of the other substances is the same. Side by side with the formation of the nitrites, there is a destruction of the latter substance. The optimum temperature is 60—70°. The acetic acid formed in the process has no appreciable action on the rate. In a mixture of milk, nitrite, and aldehyde at 50°, there is a small disappearance of nitrite, which is not sufficient to account for any appreciable loss in the mixture of nitrate, aldehyde, and ferment, and the reason for the small amount of nitrate formed is not yet accounted for in a satisfactory manner. A similar ferment was obtained from the liver of a calf. S. B. S.

Preparation of a Nitro-1-aminophenyl-4-arsinic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 232879. Compare this vol., i, 594).—The oxanil-4-arsinic acid previously employed for this preparation can be replaced by p-*urethanophenylarsinic acid*, $AsO(OH)_2 \cdot C_6H_4 \cdot NH \cdot CO_2Et$, needles, decomposing at 330—340°, and obtained by adding ethyl chlorocarbonate to a cooled alkaline solution of *p*-aminophenylarsinic acid. The *nitro*-compound prepared by nitrating the foregoing urethane in concentrated sulphuric acid solution crystallises from alcohol in yellow needles, and is converted by heating at 60—80° with sulphuric acid into nitro-1-aminophenylarsinic acid. F. M. G. M.

Quinine Esters of Phenylarsinic Acid Derivatives. K. J. OECHSLIN (*Philippine J. Sci.*, 1911, 6, 23—34).—Arsenophenylglycine and atoxyl have been found by Strong and Teague (*Philippine J. Sci.*, 1910, 5, 29) to be the best drugs which have possibilities as a specific against surra; they have the disadvantage, however, that the dose required to effect a cure is too nearly the lethal dose. The author has tested a number of substances (a list of which is given) for their action on trypanosomata, and in the course of the work has prepared the following quinine esters of phenylarsinic acid derivatives.

A suspension of benzoarsinic acid [*p*-carboxyphenylarsinic acid] in dry chloroform is reduced to benzoarsine dichloride by phosphorus trichloride. After evaporation to dryness in a vacuum on the water bath, chloroform and phosphorus pentachloride (1 mol.) are added to the residue, and the resulting solution is treated with quinine in chloroform, whereby ultimately is obtained the quinine *ester* of benzoarsine dichloride, $C_{20}H_{23}ON_2 \cdot CO_2 \cdot C_6H_4 \cdot AsCl_2$. This substance shows an exceedingly high toxicity for trypanosomata *in vitro*, but on the other hand is equally toxic for the cells of the host *in vivo*, and therefore cannot be used therapeutically. It is oxidised by hydrogen peroxide and hydrochloric acid to the quinine *ester* of benzoarsinic acid, $C_{20}H_{23}ON_2 \cdot CO_2 \cdot C_6H_4 \cdot AsO(OH)_2$, a heavy, white powder, soluble in acids or alkalis, its solutions in the former being fluorescent.

In a somewhat similar manner, di-*p*-benzoarsinic acid is converted into *diquinine dibenzoarsinate*, $C_{54}H_{55}O_8N_4As$, a fine, white powder, and phenylglycinearsinic acid through its acetyl derivative into *quinine acetylphenylglycinearsinic acid*, a heavy, white powder, which is easily soluble in dilute hydrochloric acid, aqueous ammonia, sodium hydroxide, or sodium carbonate. C. S.

Organic Chemistry.

New Catalytic Reaction with Finely Divided Nickel. H. VAN BERESTEYN (*Bull. Soc. chim. Belg.*, 1911, 25, 293—300).—In attempting to prepare heptyl alcohol from heptaldehyde by the general method of Sabatier and Senderens (compare Abstr., 1905, i, 333), the author, whilst obtaining some of the required alcohol, observed in addition the formation of considerable quantities of *n*-hexylene. This hydrocarbon was also obtained by passing heptyl alcohol over finely divided nickel, in an atmosphere of hydrogen, at 220°, this being the optimum temperature. The reaction is represented by the following equation: $C_7H_{15}\cdot OH = C_6H_{12} + CH_3\cdot OH$.

The methyl alcohol formed is decomposed in the reaction into hydrogen and carbon monoxide, the latter being detected in the gaseous products. W. G.

Optical Investigation of Argentine Petroleum. MICHAEL A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 792—793).—Crude Tartahal (Argentine) naphtha is polarimetrically semi-transparent, and the carbonisation constant *K* is greater than 1%, this being in complete correspondence with the small depths of the deposits. Various other specimens of Argentine petroleum were examined.

T. H. P.

Optical Investigation of Petroleum from Southern Bolivia. MICHAEL A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 791—792). —Two petroleums from the Yacuiba district of S. Bolivia were found to be virtually optically inactive, and to give no reaction with Tschugaeff's cholesterol reagent, trichloroacetic acid. These properties indicate a modification in the properties of the natural petroleum, as originally formed, by a process of filtration. T. H. P.

Presence of Cholesterol in Petroleum. A. K. KOSS (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 697—707).—The author has made a number of experiments with Ledok and Gogor petroleums (from Java), the results being in disagreement with Engler's view that the optical activity of petroleum is due to a product of the destructive distillation of cholesterol. For instance, when cholesterol was dissolved in a lævorotatory fraction of either of these petroleums and the solution completely distilled, the lævorotation of the distillate was found to be identical with that of the original fraction. Also, the magnitudes of the lævorotations are not altered by treatment of these fractions with ozone. T. H. P.

Borislav Ozokerite. A. K. KOSS (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 846—855).—Owing to the difficulty of separating the paraffins unchanged from ozokerite by distillation, the author has

used the extraction method, ether, which dissolves part of the asphaltene and the paraffins of lower boiling point, being used first, and the residue being then extracted with acetone. The portion extracted by the latter is divided into several fractions of varying solubility in acetone. The products were suitably purified before examination. Both the liquid and the solid portions of the ozokerite are found to be free from cholesterol.

If the ozokerite exhibits any optical activity, the active constituents belong exclusively to the liquid portion, boiling at 229—305°/10·5 mm. The rotations observed are very slight and are dextrorotations. The higher the m. p. of the paraffin, the higher is the specific gravity and the lower the degree of unsaturation (iodine number). Also, as the degree of unsaturation of the paraffin fractions diminishes, the dispersion decreases and the refraction increases.

According to Krafft, the specific gravities of normal paraffins at their melting points are almost constant, the value of ΔD being very small. With the paraffin fractions under examination, the increase of specific gravity with rise of melting point is much greater than for the normal paraffins, so that isoparaffins are probably present.

T. H. P.

Fluorobromo-derivatives containing Two Atoms of Carbon. V. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1911, 563—589. Compare *ibid.*, 1897, 33, 439, and Abstr., 1898, i, 457; 1899, i, 254; 1902, i, 129; 1909, i, 689; 1910, i, 293).—The author has prepared a series of isomeric compounds derived from *as*-tetrabromoethane. A modification of his former method of preparing tribromoethane is given, by which the vinyl bromide formed is separated, collected, and distilled on to the calculated quantity of bromine to give tribromoethane. This is then converted into *as*-dibromoethylene by boiling in alcoholic solution with potassium carbonate and potassium acetate for thirty-six hours. The resulting product after distillation out of contact with air gives on bromination the required *as*-tetrabromoethane, b. p. 112·5°/18 mm. The action of antimony fluoride on this substance is similar to that on bromoform, but is markedly different from that on either *s*-tetrabromoethane or tribromoethane. The reaction with antimony fluoride is somewhat complex. By using $\frac{1}{3}$ mol. of this reagent for every mol. of tetrabromoethane, working at 135°, the principal product is fluorotribromoethane. The other products of the reaction are tetrabromoethylene, and a liquid, b. p. 206—209°, which appeared to be fluorotetrabromoethane.

By using $\frac{2}{3}$ mol. antimony fluoride the principal product is difluorodibromoethane, $CF_2Br{\cdot}CH_2Br$. The other products are trifluorobromoethane, difluorotribromoethane, pentabromoethane, fluorotetrabromoethane, and tetrabromoethylene.

α-Fluoro-$\alpha\alpha\beta$-tribromoethane (Abstr., 1909, i, 690) is a colourless liquid, b. p. 162·7°/757 mm., $D^{17·5}$ 2·6054, $n_D^{17·5}$ 1·50215; when acted on by potassium ethoxide in an atmosphere of hydrogen, it yields α-fluoro-$\alpha\beta$-dibromoethylene, CFBr:CHBr, b. p. 88·8°, $D^{17·5}$ 2·2890. On leading oxygen into this substance, *dibromoacetyl fluoride* is produced. Alcohol decomposes this, giving ethyl dibromoacetate.

Another method is given for the preparation of fluorobromoethylene (compare *Bull. Acad. roy. Belg.*, 1909, 709) by the action of zinc dust on fluorotribromoethane. The whole operation is conducted in the absence of air, and the product so obtained has b. p. 6·8°, and can be kept in a sealed tube without showing any signs of alteration after eighteen months.

αα-Difluoro-β-bromoethylene, CF_2:CHBr, is obtained by boiling an alcoholic solution of difluorodibromoethane with potassium carbonate and potassium acetate. It is a colourless liquid, b. p. 6·2°, D^0 1·82, and is not acted on by air.

Difluorobromodiethyl ether, $CF_2Br\cdot CH_2\cdot OEt$, obtained by the action of sodium ethoxide on difluorodibromoethane, is a colourless liquid with a pungent odour, b. p. 114—115°, which on oxidation with nitric acid yields bromoacetic and hydrofluoric acids.

α-Fluoro-ααββ-tetrabromoethane, $CFBr_2\cdot CHBr_2$, a colourless liquid, b. p. 211°, or 106·4°/24 mm., $D^{17·5}$ 2·9094, results from the action of bromine on the above fluorodibromoethylene.

αα-Difluoro-αββ-tribromoethane, $CF_2Br\cdot CHBr_2$, a colourless liquid, b. p. 143·4—143·5°/754 mm., $D^{17·5}$ 2·60769, $n_D^{17·5}$ 1·50215, is obtained by the bromination of αα-difluoro-β-bromoethylene. On treatment with potassium ethoxide in an atmosphere of nitrogen, it yields *difluorodibromodiethyl ether*, $CHBr_2\cdot CF_2\cdot OEt$, a mobile liquid, b. p. 67·2°/25 mm., $D^{17·5}$ 1·9158, giving with nitric acid, hydrofluoric and dibromoacetic acids.

The author attempted to prepare a tetra-substituted ethylene by the action of potassium carbonate and potassium acetate on difluorotribromoethane. The greater portion of the product was the above ether, and only a small amount of *αα-difluoro-ββ-dibromoethylene* was obtained, which, being difficult to purify, was brominated, giving *αα-difluoro-αβββ-tetrabromoethane*, $CF_2Br\cdot CBr_3$, a solid, m. p. 99°, b. p. 185°, having a camphor-like odour. A mixture of antimony fluoride and bromine had practically no action on it.

ααβ-Trifluoro-β-bromoethane, one of the by-products in the action of antimony fluoride ($\frac{2}{3}$ mol.) on tetrabromoethane, is obtained by the action of silver fluoride on αα-difluoro-αβ-dibromoethane in sealed tubes at 120°, as a liquid, b. p. 24·8—25°. It does not react with either mercuric oxide and water at 130°, or with potassium ethoxide at 40°. When treated with sodium methoxide at 150° for seven hours, it gives *methyl trifluoroethyl ether*, $CH_2F\cdot CF_2\cdot OMe$, b. p. 45°.

The group :CF_2 imparts inertia to the molecule, as is shown by the fact that, whereas αβ-difluoro-αββ-tribromoethane, $CFBr_2\cdot CHFBr$, can be fluorinated, the corresponding ααβ-trifluoro-αβ-dibromoethane, $CF_2Br\cdot CHFBr$, cannot be so acted on. Similarly, the bromine atom in the chain $\cdot CF_2Br$ has very little mobility, and cannot be displaced by potassium ethoxide.

Further, in the ethylenes this group :CF_2 gives stability. The compounds CF_2:CH_2 and CF_2:CHBr do not undergo oxidation in air, whilst the compounds CBr_2:CH_2 and CFBr:CHF are oxidised readily. On the other hand, the group :CFBr seems the most reactive towards oxygen, and in the compound CF_2:CFBr, the group :CF_2 cannot inhibit the oxidising action on the group :CFBr.

If the general structure of the molecule remains unaltered, the transposition of fluorine and bromine atoms has little or no effect on the b. p. and density of the compound. W. G.

Action of Some Organic Acids on Sodium Formate. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1911, 440—442).—By the dry distillation of sodium formate mixed with either malonic, succinic, or tartaric acids in the requisite molecular proportions, formic acid passes over, and may be recognised by its reducing power or by the formation of ethyl formate. Tartaric acid is the least active of the three acids, and, in the case of malonic acid, acetic acid can also be found in the distillate. W. G.

Action of Some Organic Acids on Sodium Formate. II. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1911, 590—591. Compare preceding abstract).—Benzoic and tannic acids readily, gallic acid moderately, the three isomeric hydroxybenzoic acids and cinnamic acid feebly, *p*-nitrobenzoic acid partly, if the operation is carefully conducted, and malic acid only partly, displace formic acid from sodium formate on dry distillation.

Incidentally the author notes certain points as to the behaviour of cinnamic acid on sublimation and dissolution, and mentions ethyl alcohol or pure methyl alcohol as the best solvents for it. W. G.

The Optically Active Modifications of Lactic Acid. REGINALD O. HERZOG and P. SLANSKY (*Zeitsch. physiol. Chem.*, 1911, **73**, 240—246).—Jungfleisch (Abstr., 1904, i, 645) has stated that the two optically active modifications of lactic acid are racemised in alkaline solution at different rates. The two modifications have now been prepared with the aid of morphine by Irvine's method (Trans., 1906, **89**, 935), and heated both in alkaline acid and neutral solution. The rotations were determined in presence of ammonium molybdate under standard conditions. No difference whatever was found in the behaviour of the two antipodes. E. F. A.

Electrolytic Reduction of Lævulic Acid and α-Dimethyl-lævulic Acid. JULIUS TAFEL and BRUNO EMMERT (*Zeitsch. Elektrochem.*, 1911, **17**, 569—572).—Alkaline solutions of the acids were reduced at a prepared lead cathode at about 20° with a current density of about 0·12 ampere per sq. cm. (Abstr., 1900, ii, 588). With acid solutions, it was necessary to add alcohol in order to prevent the formation of a non-conducting film of valeric acid on the lead cathode, or else to use a cathode of mercury instead of lead.

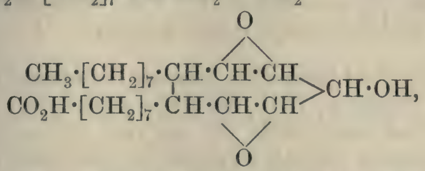
Lævulic and dimethyl-lævulic acid are reduced in alkaline solutions to the corresponding hydroxy-acids or lactones.

In acid solutions lævulic acid is reduced to valeric acid, but dimethyl-lævulic acid yields the corresponding lactone as the principal product, only small quantities of dimethylvaleric acid being formed.

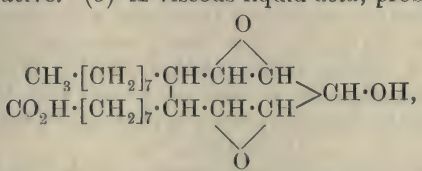
Hydroxyvaleric acid, valerolactone, and α-dimethylvalerolactone are not reduced at all under the conditions used, and these substances cannot therefore be regarded as intermediate products in the reduction to the fatty acids. T. E.

Reactions of Certain Unsaturated Fatty Acids with Formaldehyde. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 809—819).—The author has studied the compounds obtained by the condensation of oleic, elaidic, and undecoic acids with formaldehyde in presence of sulphuric acid. It is found that more definite and non-polymerised products are obtained if the reaction is carried out at low temperatures.

With oleic and elaidic acids the products seem to be identical, and consist of the following acids: (1) A white, crystalline *compound*, $C_{21}H_{40}O_4$ or $\begin{matrix} CH_3\cdot[CH_2]_7\cdot CH\cdot CH(OH) \\ CO_2H\cdot[CH_2]_7\cdot CH\cdot CH(OH) \end{matrix} > CH_2$ (?), m. p. 112—114° (110—113·5°), solidifying at 102—97° (100·5—94°); the iodine number is 7·6, which indicates the absence of double linkings. The *sodium* and *silver* salts and the *diacetyl* derivative were prepared. (2) An *acid*, $\begin{matrix} CH_3\cdot[CH_2]_7\cdot CH\cdot CH_2\cdot O\cdot CH_2 \\ CO_2H\cdot[CH_2]_7\cdot CH\cdot CH_2\cdot O\cdot CH_2 \end{matrix} > CH\cdot OH$ or

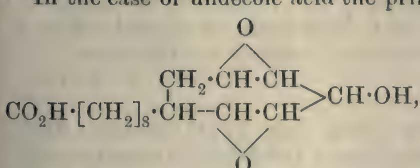


which was obtained as a liquid soluble in light petroleum, and forms a *monoacetyl* derivative. (3) A viscous liquid *acid*, probably



having a bitter taste; it is insoluble in light petroleum, and forms a *monoacetyl* derivative. The *sodium* salt was analysed.

In the case of undecoic acid the principal product is a viscous *liquid*,

 soluble in ether.

T. H. P.

The Hæmolytic Action of the Fat of Rice (Oryza sativa, L.) Hæmolysis of Fatty Acids. J. SHIMAZONO (*Arch. expt. Path. Pharm.*, 1911, 65, 361—366).—The alcoholic and ethereal extracts of rice possess hæmolytic properties which the author traced to the palmitic acid present. This observation led him to study the hæmolytic powers of other fatty acids; working upwards from formic acid, these properties were absent in the lower members, and did not appear until nonoic acid was reached. The higher acids were markedly hæmolytic. It thus appears possible that the hæmolytic

action of various organs vaguely ascribed to lipoids, etc., may in reality be due to higher fatty acids. E. J. R.

Cochineal Fat. R. HUERRE (*J. Pharm. Chim.*, 1911, [vii], 4, 56—65).—The fat extracted by boiling ether from "silver cochineal" has m. p. 32°, iodine number 50·53, and the percentage composition free fatty acids 89, glycerides 8, and unsaponifiable matter 3. Liebermann has shown already that the saturated acid present is myristic, and the author finds that the liquid acids are composed of oleic 35% and linoleic 8%, calculated on the "total fatty acids." Oleic acid was isolated by means of the lead salt, but attempts to isolate the linoleic acid in a pure state by Farnsteiner's method (Abstr., 1899, ii, 705) and by the process Haller has used for the separation of oleic acid from saturated fatty acids (Abstr., 1907, i, 9, 10) were unsuccessful, and the presence of linoleic acid was proved by the detection of tetrahydroxystearic acid in the products of oxidation of the liquid fatty acids by permanganate. The unsaponifiable matter is orange-coloured, and has a high iodine number. T. A. H.

Fatty Acids of Cod-liver Oil. ALFRED HEIDUSCHKA and E. RHEINBERGER (*Pharm. Zentr.-h.*, 1911, 52, 837—838).—It has been shown previously that the fatty acids of cod-liver oil on treatment with Hübl's iodine solution furnish a crystalline derivative, $C_{17}H_{26}O_2Cl_4I_4$, of terapic acid, $C_{17}H_{26}O_2$, in which the iodine can be replaced by chlorine, forming terapic acid octachloride (Abstr., 1910, i, 297).

The first of these derivatives on treatment with zinc and acetic acid furnishes an *acid*, $C_{17}H_{28}O_2$, as a nearly colourless oil, distilling at 154°/75 mm., and having iodine number 264·5. When terapic acid tetrachloride tetraiodide is treated with bromine, the four iodine atoms are replaced by bromine atoms, giving the *compound*,

$$C_{17}H_{26}O_2Cl_4Br_4,$$

m. p. 150°, which forms a yellowish-brown, crystalline powder, soluble in the usual organic solvents.

Terapic acid octachloride forms a *potassium* salt. *Linolenic acid trichloride tri-iodide*, $C_{18}H_{30}O_2Cl_3I_3$, m. p. 95°, formed by the action of Hübl's iodine solution on the mixed fatty acids of linseed oil, is a colourless, crystalline substance, soluble in alcohol or chloroform. T. A. H.

Soya Bean Oil. S. KEIMATSU (*Chem. Zeit.*, 1911, 35, 839—840). —The oil used had the following constants: D^{15} 0·9265, viscosity at 20° 8·9 to 9·0 (Engler's apparatus), solidifying point −15° to −16°, m. p. −7° to −8°, solidifying point of fatty acids 16—17°, m. p. of fatty acids 23—24°, saponification number 190, iodine value 132—135, and Hehner number 94·2. It contained 0·2% of a phytosterol, m. p. 136—137°, which was not stigmasterol. The fatty acids were separated into saturated and unsaturated by means of the lead salts. The former included palmitic and stearic acids (together 12%). The unsaturated acids on oxidation furnished *iso*linusic, dihydroxystearic, and sativic acids, together with an isomeride of sativic acid, m. p. 158—159° (compare Hartley, Abstr., 1909, ii, 597), and an unidentified

acid, m. p. 145—149°, probably impure. These oxidation products indicate the presence in the oil of the following acids, *iso*linolenic, oleic, linoleic (these two together 15%), and an isomeride of linoleic acid (50%). T. A. H.

Preparation of Oxalic Acid by the Fusion of Sawdust with Potassium Hydroxide. A. VON HEDENSTRÖM (*Chem. Zeit.*, 1911, **35**, 853—854).—There being no exact details as to yields, temperature of fusion, etc., in the manufacture of oxalic acid from sawdust, the author has carried out the following experiments, using, in the preliminary work, purified cotton wool instead of sawdust.

Three grams of cotton-wool were heated with 12 grams of potassium hydroxide and 20 c.c. of water in a nickel crucible on a sand-bath, the temperature of the mass being carefully taken. The best yield, 3·72 grams of oxalic acid, was obtained when the temperature was gradually raised to, and maintained at, 280° until no further reaction took place, the fusion then being cooled with continuous stirring. The yield is much less, 1 gram, when the temperature does not exceed 225°, even on prolonged heating. The addition of potassium oxalate in small quantity, as also of potassium permanganate or lead peroxide, further increases the yield of oxalic acid at 280°; the passage of air through the fusion has a similar effect.

Three grams of oak sawdust gave similar results and yields to the cotton-wool. It is thus probable that the lignin substances give oxalic acid as well as the cellulose, and this was confirmed by first extracting the sawdust with a 10% solution of potassium hydroxide at the ordinary temperature, filtering, evaporating the filtrate to dryness, and fusing the residue at 280°. 1·27 Grams of oxalic acid were obtained, which, together with 2·36 grams of oxalic acid obtained from the residual sawdust after extraction, give 3·63 grams, which is practically the same yield as 3·66 grams obtained by direct fusion of 3 grams of sawdust. No oxalic acid was obtained by the extraction of cotton-wool with 10% potassium hydroxide. T. S. P.

Stereoisomeric Dihalogensuccinic Acids. BROR HOLMBERG (*J. pr. Chem.*, 1911, [ii], **84**, 145—168).—The author has measured the velocity of decomposition of dibromosuccinic, *iso*dibromosuccinic, dichlorosuccinic, and *iso*dichlorosuccinic acids, and also of their normal and acid barium salts in (1/30 molar) aqueous solution at 25°, by determining the increase of acidity by means of standard alkali, and finds that the reactions are all of the unimolecular type. The close agreement in the values obtained for the velocity constants indicates that the decomposition of the acids is not affected by the presence of the halogen acid formed in the reaction, and this is confirmed by the comparatively small differences in the constants, obtained for the decomposition of one and the same acid (1) in aqueous solution, (2) in the presence of hydrochloric acid, (3) in the form of its barium hydrogen salt. Although Lossen and Reisch (Abstr., 1898, i, 357) have shown that several reactions take place simultaneously during the decomposition of dibromosuccinic acid in aqueous solution, under

the conditions chosen by the author the decomposition occurs mainly according to the scheme:

$$O\cdot CO\cdot CHBr\cdot CHBr\cdot CO\cdot O'' = O\cdot CO\cdot CH\dot{:}CBr\cdot CO\cdot O'' + H^{\circ} + Br'.$$

The behaviour of the isomeric dibromosuccinic acids towards potassium sulphide, potassium xanthate, sodium ethyl sulphide, and potassium trithiocarbonate has also been investigated. When dibromosuccinic acid, in the form of its sodium salt, is allowed to react with these substances in aqueous solution, it is almost quantitatively transformed into fumaric acid, whilst the *iso*-acid, under the same conditions, reacts with difficulty, yielding mainly bromofumaric acid.

Measurements have also been made of the electrical conductivity of the acids and their sodium hydrogen salts, and also of the hydrogen-ion concentration of the same substances in aqueous solution by Bredig and Fraenkel's method (Abstr., 1905, ii, 692); from the results thus obtained, the following values for the primary (k) and secondary (s) affinity constants of the acids have been calculated: dichlorosuccinic acid, $k = 0{\cdot}03$, $s = 8{\cdot}1$; *iso*dichlorosuccinic acid, $k = 0{\cdot}035$, $s = 9{\cdot}9$; dibromosuccinic acid, $k = 0{\cdot}037$, $s = 13{\cdot}6$; *iso*dibromosuccinic acid, $k = 0{\cdot}37$, $s = 4{\cdot}3$.

Unsuccessful attempts to resolve dibromosuccinic acid by crystallisation of the alkaloidal salts are recorded.

The *cinchonine* salt, $C_{42}H_{48}O_6N_4Br_2,6H_2O$, and *strychnine* salt,

$$C_{21}H_{22}O_2N_2,C_4H_4O_4Br_2,$$

are described. F. B.

Formation of Cork. S. ZEISEL (*J. pr. Chem.*, 1911, [ii], 84, 317—323).—The author criticises adversely the work of Schmidt (Abstr., 1910, i, 540) on this subject, and maintains that the latter's experiments lend no support to the view that cork is produced by the formation of anhydrides and polymerisation of fatty acids, originally present in young cork in the form of glycerides. F. B.

Sulpho-ethereal Salts or Thionic Esters, R·CS·OR'. MARCEL DELÉPINE (*Compt. rend.*, 1911, 153, 279—282. Compare Abstr., 1910, i, 295).—The following thionic esters have been prepared by the method already indicated (Abstr., 1910, i, 612), or by Matsui's process (Abstr., 1909, i, 463). Experimental details are given for the former.

Ethyl thionacetate, $CH_3\cdot CS\cdot OEt$, b. p. 109—110°, D_4^0 0·9816. Ethyl thionpropionate, b. p. 130—132°, D_4^0 0·9639. *Methyl thion*iso*butyrate*, b. p. 145—148°, D_4^0 0·9577; the *ethyl* ester has b. p. 160—165°, D_4^0 0·9549. *Methyl thion*iso*valerate*, b. p. 160—170° (?). *Methyl thionoctoate*, b. p. 115—120°/12 mm. *Methyl thionbenzoate*, b. p. 110—112°/10 mm. *Methyl thion*cyclo*hexoate*, b. p. 90—100°/12 mm. The last four compounds were not obtained perfectly pure.

The methyl and ethyl esters fume in the air, are strongly phosphorescent, and have an ozone-like odour up to the C_5 terms. The thionbenzoates are also phosphorescent. The higher members of the series as well as the hydroaromatic compounds do not show these properties. W. O. W.

Photochemical Synthesis of Carbohydrates in Absence of Chlorophyll. JULIUS STOKLASA and VENCESLAS ZDOBNICKY (*Bull. Assoc. Chim. Sucr. Dist.*, 1911, **29**, 26—31).—In presence of potassium hydroxide, carbon dioxide and nascent hydrogen interact with production of formic acid. Under the influence of ultra-violet rays a sugar is formed.

Formaldehyde is produced by the interaction of water vapour and carbon dioxide in presence of potassium hydroxide and ultra-violet rays.

Negative results were obtained by submitting (1) water vapour and carbon dioxide, and (2) carbon dioxide, nascent hydrogen, and potassium hydroxide to the action of ultra-violet rays. N. H. J. M.

Instability of Dextrose at the Temperature and Alkalinity of the Body. LAWRENCE J. HENDERSON (*J. Biol. Chem.*, 1911, **10**, 3—7).—It is suggested that the very exact regulation of the alkalinity of the body has as one of its principal objects the preservation of a suitable medium for the destruction of dextrose and the regulation of the process. When dextrose is boiled with a mixture of sodium hydrogen phosphate and disodium hydrogen phosphate in varying proportions, the mixture becomes optically inactive within a few hours. Similar solutions preserved with toluene in sealed flasks at 38° for forty-four days showed a slight loss in optical activity.

E. F. A.

Action of Sodium and Potassium Hydroxides on the Optical Behaviour of Dextrose in Solution. S. C. PROFILO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iiia], **17**, 174—181).—In the presence of a fairly high concentration of sodium or potassium hydroxide, a solution of dextrose, which is at first dextrorotatory, slowly diminishes in optical activity and becomes lævorotatory; after a long interval, the lævorotation has diminished to such an extent that the solution is optically neutral. It is suggested that a equilibrium mixture of dextrose, lævulose, and mannose is finally formed, represented by the equation: dextrose $\rightleftarrows$ lævulose $\rightleftarrows$ mannose, and that the sign of the rotation depends on the relative proportions of these substances present. It is possible that after a time the mixture would again become dextrorotatory, but readings ultimately become impossible owing to the depth of colour of the solution. G. S.

Behaviour of Sucrose and its Decomposition Products on Heating. J. E. DUSCHSKY (*Zeitsch. Ver. deut. Zuckerind.*, 1911, 855—879. Compare this vol., i, 607).—Concentrated sucrose solutions of alkaline reaction withstand heating at temperatures up to 130° without appreciable decomposition, as measured either by a fall in the polarisation or by the formation of reducing substances. In cases where a change does take place in solutions which were originally alkaline, it is found that the alkalinity has been destroyed by acid decomposition products, which subsequently facilitate a complete decomposition. Excess of alkali and the nature of the alkali have no influence on the decomposition of concentrated sucrose solutions.

When the reaction is acid, decomposition ensues without any

regularity, and its amount is not proportional to the time or temperature of heating. At first dextrose and lævulose are formed, and these are further changed to a series of optically active and inactive substances.

Both in concentrated and in dilute solution the decomposition of sucrose is facilitated before all by the reaction of the medium, and then by the temperature and period of heating. The influence of concentration is subordinate and very irregular.

The quantitative results of heating sucrose solutions of alkaline reaction of 50% to 75% concentration for one hour at temperatures from 80° to 135° are contained in a series of tables which give the amount of sugar lost by the process. Heating has but little influence up to 110°; at higher temperatures the loss increases rapidly, amounting to 0·2% to 0·3% at 120°. This indicates that it is inadvisable to warm sugar solutions above a certain limit, and the determinations of the destruction of alkali on heating, which are also tabulated, point to the same conclusion. E. F. A.

Empirical Relation between the Configuration and Rotation of Sugars. Ernest Anderson (*J. Amer. Chem. Soc.*, 1911, 33, 1510—1514).—The direction and degree of optical rotation of the sugars are determined by the configuration of the α- and β-carbon atoms. The four possible configurations with their corresponding rotations are:

$$\begin{array}{lll} \text{OH} & \text{H} & \\ \cdot\text{C}— & \text{C}\cdot\text{CHO} & = \text{strongly dextrorotatory.} \\ \text{H} & \text{OH} & \end{array}$$

$$\begin{array}{lll} \text{H} & \text{OH} & \\ \cdot\text{C}— & \text{C}\cdot\text{CHO} & = \text{strongly lævorotatory.} \\ \text{OH} & \text{H} & \end{array}$$

$$\begin{array}{lll} \text{OH} & \text{OH} & \\ \cdot\text{C}— & \text{C}\cdot\text{CHO} & = \text{slightly dextro- or lævo-rotatory.} \\ \text{H} & \text{H} & \end{array}$$

$$\begin{array}{lll} \text{H} & \text{H} & \\ \cdot\text{C}— & \text{C}\cdot\text{CHO} & = \text{slightly dextro- or lævo-rotatory.} \\ \text{OH} & \text{OH} & \end{array}$$

It is claimed that this applies to all sugars for which both configuration and rotation are known. The theory is applied to the determination of configuration when the rotatory power is known.

E. F. A.

Action of Oxalic and Malonic Acids on Starch and Dextrin. William Oechsner de Coninck and A. Raynaud (*Bull. Acad. roy. Belg.*, 1911, 438—439. Compare this vol., i, 423, 607).—With these two dibasic acids the amount of hydrolysis is proportional to the concentration of the acids, and the quantity of dextrin hydrolysed is always greater than that of starch hydrolysed. In the latter respect the two acids under consideration resemble the mineral acids already studied, and differ from the monobasic formic and acetic acids. W. G.

Action of Lactic and Tartaric Acids on Starch and Dextrin. WILLIAM OECHSNER DE CONINCK and A. RAYNAUD (*Bull. Acad. roy. Belg.*, 1911, 592—593. Compare this vol., i, 423, 617, and preceding abstract).—In the case of these two hydroxy-acids the rates of hydrolysis for starch and dextrin are practically the same, the two acids thus resembling formic and acetic acids in their behaviour.

The conclusion drawn from the whole series of experiments is that the rate of saccharification, per molecule of acid, is three or four times greater with mineral than with organic acids. W. G.

New Solvents for Cellulose and their Action on this Substance. HORACE G. DEMING (*J. Amer. Chem. Soc.*, 1911, **33**, 1515—1525).—Cellulose in the form of filter paper is soluble in concentrated aqueous solutions of antimony trichloride, stannous chloride, and zinc bromide. When dissolved in the halogen acids (hydrochloric acid, etc.), these salts and many others dissolve cellulose with great ease. A few salts in solution in formic or trichloroacetic acids also act as solvents for cellulose.

Cellulose attracts metallic salts in solution, forming an adsorption complex, and the salt is distributed between the fibre and the solution. When an agent is present which, like certain dilute acids, can bring about union with water, the complex is brought into solution.

In proof of this view much evidence is adduced. Cellulose modified by acids becomes soluble in aqueous calcium chloride solutions which cannot dissolve pure cellulose. Chlorosulphonic, arsenic, and selenic acids are able to dissolve cellulose.

Celluloses dissolved in acid solutions of salts are precipitated on pouring into water as amorphous compounds with marked reducing properties and easily hydrolysed.

One of the formates of cellulose when hydrolysed by concentrated hydrochloric acid is converted into compounds soluble in water, and finally into dextrose. E. F. A.

β-Aminoethyl Alcohol, a Product of the Hydrolysis of the Lecithin of Bean Meal. GEORG TRIER (*Zeitsch. physiol. Chem.*, 1911, **73**, 383—388).—β-Aminoethyl alcohol is obtained among the products of the hydrolysis of the phosphatide of bean meal (*Phaseolus vulgaris*) with barium hydroxide, and proved to be in all respects identical with the synthetic product. β-Aminoethyl alcohol is regarded as the parent substance of choline, which is evidently derived from it by complete methylation in the plant. E. F. A.

Homocholine and Neosine. E. BERLIN (*Zeitsch. Biol.*, 1911, **57**, 1—74).—The chief point of chemical interest is a comparison of the homocholines obtained by various investigators. The author decides that Malengreau and Lebailly's β-homocholine (Abstr., 1910, i, 545) is identical with Morley's (Abstr., 1881, 151; Morley and Green, *Ber.*, 1885, **18**, 24), and that the constitution $OH\cdot NMe_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$ of Weiss' (*Zeitsch. Naturwiss.*, 1887, **60**, 221) and of Schmidt and Partheil's (Abstr., 1892, 950) γ-homocholine is not proved. The author has prepared γ-homocholine (*mercurichloride*,

$$C_6H_{16}ONCl,6HgCl_2,$$

m. p. 208°; *picrate*, m. p. 255°) by the same method as Malengreau and Lebailly (*loc. cit.*), and has proved its constitution by oxidising it to β-homobetaine by calcium or barium permanganate and warm dilute sulphuric acid. He finds that its aurichloride has m. p. 193—194°, whereas Malengreau and Lebailly give 183°. In consequence of this discrepancy, the author prepares γ-homocholine by another process, and has thereby cleared away much of the confusion in the literature of the homocholines. By exhaustive methylation, γ-aminopropyl alcohol yields two homocholines, which are separated best by means of their mercurichlorides. The less soluble fraction, m. p. 203°, of the mercurichlorides yields an aurichloride, m. p. 187—190°, the base in which is proved to be γ-homocholine by its oxidation to β-homobetaine. The more soluble fraction, m. p. 208°, of the mercurichlorides yields an aurichloride, m. p. 163° [the same as that of Weiss' and of Schmidt and Partheil's γ-homocholine aurichloride (*loc. cit.*)], the base in which is proved to be β-homocholine by its oxidation to betaine. Consequently the so-called γ-homocholine of these two investigators is in reality β-homocholine. A feasible explanation is given for the production of β-homocholine in Schmidt and Partheil's method, and also in the author's second process (above). A discrepancy, as yet unexplained, still remains; Malengreau and Lebailly (*loc. cit.*) give the m. p. of β-homocholine aurichloride as 195—196°.

By-products in the preparation of γ-homocholine from trimethylamine and trimethylene chlorohydrin are the *ether* of γ-homocholine [*platinichloride*, $O(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3)_2,PtCl_6$, m. p. 253—254°; *aurichloride*, $C_{12}H_{30}ON_2,2AuCl_4$, m. p. 230—232°] and hexamethyltrimethylenediammonium hydroxide [*platinichloride*,

$$C_9H_{24}N_2,PtCl_6,H_2O,$$

m. p. 258—260° (decomp.)]; the latter is also formed in the author's second process.

Neosine has been isolated from shrimps by Kutscher and Ackermann's method (Abstr., 1908, i, 675). It contains choline, the removal of which is very difficult, but sufficient pure material has been obtained to show, by a comparison of the platinichlorides, mercurichlorides, and aurichlorides, that neosine is not identical with γ-homocholine (compare Kutscher and Ackermann, *loc. cit.*).

Two points of physiological interest are discussed. Firstly, it is shown that γ-homocholine chloride is decidedly more poisonous than choline chloride; thus is disproved Meyer and Schmidt's statement (Abstr., 1905, i, 23) that the physiological activity of the base is weakened when the side-chain is lengthened. Secondly, there has been a controversy as to whether the lowering of the blood-pressure by the injection of choline chloride is due to the substance itself or to an impurity therein. The former view is supported by the author's experiments, since synthetic choline chloride, γ-homocholine chloride, and β-homocholine chloride (in which the presence of such an impurity is almost impossible) all cause a lowering of the blood-pressure. It is remarkable that γ-homocholine ether and hexamethyltrimethylenediammonium dichloride are, comparatively, non-poisonous.

C. S.

d-α-Aminobutyric Acid and l-α-Aminobutyrylglycine. ARTHUR H. KOELKER (*Zeitsch. physiol. Chem.*, 1911, 73, 312—313).—r-α-Aminobutyrylglycine has been asymmetrically hydrolysed by means of an active enzyme in yeast into d-α-*aminobutyric acid*, $[\alpha]_D^{20}$ $+9°$, glycine, and l-α-*aminobutyrylglycine*, $[\alpha]_D^{20}$ $-86{\cdot}4°$. E. F. A.

Production of Some Amino-acids from the Phenylhydrazones of Ketonic Acids by Aluminium Amalgam, and Preparation of the Optically Active γ-Aminovaleric Acids. EMIL FISCHER and REINHART GROH (*Annalen*, 1911, 383, 363—372). —When reduced in alcoholic solution by aluminium amalgam and water, the phenylhydrazones of lævulic acid, ethyl acetoacetate, and pyruvic acid yield γ-aminovaleric acid, β-aminobutyric acid (best method of preparation), and alanine respectively in 55—60% yield.

r-γ-Aminovaleric acid, in the form of its benzoyl derivative, is easily resolved by quinine. d-γ-*Benzoylaminovaleric acid*, $C_{12}H_{15}O_3N$, has m. p. 133° (corr.), $[\alpha]_D^{20}$ $-21{\cdot}9°$ in alcohol, and is less soluble in water than the racemic form. When hydrolysed by 20% hydrochloric acid on the water-bath, it yields d-γ-*aminovaleric acid*, m. p. 214° (corr., decomp.), and $[\alpha]_D^{20}$ $12{\cdot}0°$ in water. l-γ-*Benzoylaminovaleric acid*, containing some of the racemic form, has $[\alpha]_D^{20}$ $16{\cdot}5°$ in alcohol, and yields an impure l-*aminovaleric acid*, having $[\alpha]_D^{20}$ $-10{\cdot}7°$ in water. C. S.

Preparation of the Free Esters of Amino-acids. NICOLAI ZELINSKY, A. ANNENKOFF, and J. KULIKOFF (*Zeitsch. physiol. Chem.*, 1911, 73, 459—470).—The free amino-acid esters may be obtained from their hydrochlorides by heating with excess of lead hydroxide. The procedure is as follows: the hydrochlorides of the esters are prepared as usual by the action of hydrogen chloride on a solution of the amino-acid in absolute alcohol, the alcohol is evaporated in a vacuum, the residue mixed with lead hydroxide, and the mixture distilled in a vacuum, when almost pure ester is obtained with a yield of 85—95% of the possible.

Ethyl α-amino*iso*butyrate has b. p. 38·5—41°/10 mm., D_4^{17} 1·0974, n_D^{17} 1·4169.

Ethyl alanine has b. p. 49—51°/10 mm.; ethyl α-iminodipropionate obtained at the same time showed b. p. 114—115°/10 mm., D_4^{20} 1·0152, n_D^{20} 1·4728.

Ethyl 1-*amino*cyclo*pentane*-1-*carboxylate* has b. p. 80°/10 mm., D_4^{20} 1·0292, n_D^{20} 1·4531. *Ethyl* 1-*amino*cyclo*hexane*-1-*carboxylate* has b.p. 100°/14 mm., D_4^{20} 1·0182, n_D^{20} 1·4614. Both these esters are stable, and do not tend to form a diketopiperazine.

Ethyl methylaspartate is likewise very stable; it has b. p. 112·5—113°/12 mm., D_4^{20} 1·0632, n_D^{20} 1·4332. *Ethyl* α-*methylaminopropionate* has b. p. 75—76°/65 mm., D_4^{20} 1·4128, n_D^{20} 1·4218, and can be kept for months in sealed tubes without change. E. F. A.

Oxidation of the Amino-acids. II. Alanine and Tyrosine. W. DENIS (*J. Biol. Chem.*, 1911, 10, 73—76. Compare this vol., i, 616).—The products of oxidation of alanine with alkaline potassium

permanganate are ammonia, carbon dioxide, oxalic, acetic and nitric acids. Tyrosine oxidised in the same way yields ammonia, carbon dioxide, oxalic, acetic and nitric acids, with traces of an acid which is probably *p*-hydroxybenzoic. W. D. H.

Conversion of Glycine into Iminodiacetic and Triglycolamic Acids. MAX SIEGFRIED (*Zeitsch. physiol. Chem.*, 1911, **73**, 194—203. Compare this vol., i, 427).—Much of the work described has been already abstracted (*loc. cit.*).

When glycine and mercuric chloride are set aside at 37° for several days, triglycolamic acid, $N(CH_2 \cdot CO_2H)_3$, m. p. 256—257° (decomp.), is obtained.

Alanine is not altered on similar treatment with mercuric chloride. E. F. A.

Poulenc's Sodium Glycerophosphate and a Free Glycerophosphoric Acid. VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 807—812).—The sodium glycerophosphate of Poulenc is prepared by a patented process by heating monosodium phosphate and glycerol. It has the composition of a *disodium glycerophosphate*, $Na_2(C_3H_7O_2)PO_4$. This indication that it is a chemical individual is confirmed by the fact that the author has prepared pure brucine β-glycerophosphate (Tutin and Hann, Trans., 1906, **89**, 1749) in good yield from the free acid obtained from it by way of the *silver* salt. R. V. S.

The Configuration of the Benzene Nucleus. WILHELM VAUBEL (*Zeitsch. angew. Chem.*, 1911, **24**, 1759—1760).—Polemical against Lifschitz (this vol., i, 622). T. S. P.

Old and New Benzene Formulæ. ISRAEL LIFSCHITZ (*Zeitsch. angew. Chem.*, 1911, **24**, 1760).—A reply to Vaubel (compare preceding abstract). T. S. P.

Polymerisation of Diethylene Hydrocarbons. II. Polymerisation and Isomerisation of *as*-Dimethylallene. SERGIUS V. LEBEDEFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 820—835. Compare this vol., i, 26).—When *as*-dimethylallene is heated in sealed tubes at 100—225° for two to twenty days, according to the temperature, it yields dipentene, the two following dimerides, and also a trimeride, the investigation of which is now proceeding. It will be seen that these products are both derivatives of *cyclo*butane.

1 : 2-*Diisopropenyl*cyclo*butane*, $\begin{matrix} CH_2 \cdot C{:}CMe_2 \\ | \qquad | \\ CH_2 \cdot C{:}CMe_2 \end{matrix}$, is a colourless liquid with a faint, aromatic smell, b. p. 61—62°/9 mm., 179—181°/753 mm., D_4^0 0·8571, D_4^{20} 0·8422, $n_D^{19.7}$ 1·50086, $n_G^{19.7}$ 1·52345. It has the normal molecular weight in freezing benzene, and readily oxidises in the air. With nitrous acid, it gives a crystalline *substance*, m. p. 141°. When hydrogenated in presence of platinum black it yields

1 : 2-*Diisopropyl*cyclo*butane*, $\begin{matrix} CH_2 \cdot CH \cdot CMe_2 \\ | \qquad | \\ CH_2 \cdot CH \cdot CMe_2 \end{matrix}$, which is a faint smell-

ing liquid, b. p. 157—158·5°/760 mm., D_4^0 0·7901, D_4^{20} 0·7755, n_D^{20} 1·42787, n_G^{20} 1·43755. This compound is also formed, together with a decane, b. p. 153—155·5° (impure), when the hydrogenation is carried out in presence of reduced nickel at 275° and a pressure of 100 atmospheres.

The action of ozone on 1 : 2-di*iso*propenyl*cyclo*butane yields an ozonide which, when decomposed with water, gives 1-iso*propenyl*-2-cyclo*butanone*, $CH_2<\genfrac{}{}{0pt}{}{CO-}{CH_2}>C{:}CMe_2$, as a slightly yellow liquid with a strong odour, recalling that of *p*-benzoquinone, b. p. 57°/11 mm., 171°/760 mm., D_4^{20} 0·9326, n_D^{20} 1·48618, n_G^{20} 1·50571 ; it absorbs oxygen from the air. It forms a *phenylhydrazone*, yellow needles, and a *semicarbazone*, $C_{18}H_{13}ON_3$, m. p. 241°. Attempts to convert the ketone into the corresponding 1 : 2-dione resulted only in the formation of succinic anhydride and condensation products. Oxidation with nitric acid (1 : 1) gave a theoretical yield of succinic acid. In the preparation of the ozonide, the latter is accompanied by succinic anhydride, acetone peroxide, and acetone, these being evidently formed by the decomposition of an unstable diozonide.

1-iso*Propyl*-2-cyclo*butanone*, $CH_2<\genfrac{}{}{0pt}{}{CO-}{CH_2}>CHPr^\beta$, obtained by the action of hydrogen on the unsaturated ketone in presence of platinum black, has b. p. 148—150°/770 mm., D_4^{20} 0·8704, n_D^{20} 1·42827, n_G^{20} 1·43843. The *semicarbazone*, $C_8H_{15}ON_3$, m. p. 183°, was prepared.

1 : 1-*Dimethyl*-2-*methylene*-3-iso*propenyl*cyclo*butane*,

$$CMe_2<\genfrac{}{}{0pt}{}{C({:}CH_2)}{-CH_2-}>C{:}CMe_2,$$

is a colourless liquid with an odour resembling that of kerosene, b. p. 37—39°/9 mm., 149—150°/752 mm., D_4^0 0·8143, D_4^{20} 0·7982, $n_D^{19·7}$ 1·46769, n_G^{20} 1·48623. With nitrous acid it gives a crystalline product, m. p. 100° (decomp.).

1 : 1 : 2-*Trimethyl*-3-iso*propyl*cyclo*butane*, $CMe_2<\genfrac{}{}{0pt}{}{CHMe}{-CH_2-}>CHPr^\beta$, obtained by hydrogenating the preceding compound under a pressure of 35 atmospheres in presence of platinum black, is a liquid, b. p. 145—146·5°/760 mm., D_4^0 0·7744, D_4^{20} 0·7598, n_D^{20} 1·41997, n_G^{20} 1·42980.

The action of ozone on 1 : 1-dimethyl-2-methylene-3-*iso*propenyl*cyclo*butane yields various condensed products, *as*-dimethylsuccinic acid and an ozonide, which, as would be expected from the unsymmetrical character of the original hydrocarbon and the consequent formation of two mono-ozonides, gives the following two ketones (together with formic acid, acetone, and acetone peroxide) when decomposed with water.

1 : 1-*Dimethyl*-2-*methylene*-3-cyclo*butanone*, $CMe_2<\genfrac{}{}{0pt}{}{C({:}CH_2)}{-CH_2-}>CO$, is a faintly yellow liquid with a pungent odour, b. p. 59—60°/50 mm., D_4^0 0·8854, D_4^{20} 0·8684, n_D^{20} 1·44654, n_G^{20} 1·46123. It readily oxidises in the air, depositing crystals, m. p. 129°, which emit a flash of light when heated. Its *semicarbazone*, $C_8H_{13}ON_3$, has m. p. 160—190° (decomp.).

1 : 1-*Dimethyl*-3-iso*propenyl*-2-cyclo*butanone*, $CMe_2<\begin{matrix}CO-\\CH_2\end{matrix}>C:CMe_2$, b. p. 58—65°/11·5 mm., is very unstable, and was not obtained pure. T. H. P.

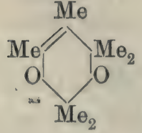
Hydrogenation in the Presence of Finely Divided Palladium. II. PIERRE BRETEAU (*Bull. Soc. chim.*, 1911, [iv], 9, 764—770. Compare this vol., i, 123).—Phenanthrene can be reduced electrolytically, using spongy palladium deposited on a platinum-iridium gauze cylinder as a cathode. The hydrogenation takes place in an alcoholic sulphuric acid solution with a current of 10 amperes and 8 volts. The tetrahydrophenanthrene after precipitation by water is extracted with ether. W. G.

Nitration of *o*-, *m*-, and *p*-Nitrobenzoyl-*p*-anisidines. FRÉDÉRIC REVERDIN (*Compt. rend.*, 1911, 153, 278—279; *Arch. sci. phys. nat.*, 1911, [iv], 32, 124—134*).—The nitro-group in the three nitrobenzoyl-*p*-anisidines is without influence on the course of nitration when these substances are treated with nitric acid, alone or in acetic acid solution. In each case, according to the conditions, orange mononitro-derivatives, yellow dinitro-derivatives, or colourless trinitro-compounds are formed. On hydrolysis, these substances give 3-nitro-, 2 : 3-dinitro-, and 2 : 3 : 6-trinitro-*p*-anisidine respectively, thus proving their constitution. The *o*-nitrobenzoyl derivatives and the trinitro-compounds are hydrolysed with ease by sulphuric acid, the others with difficulty.
W. O. W.

Crystallographic Study of Ethyl *iso*Succino-*p*-toluidate. ARISTIDE ROSATI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 921—922).—Ethyl *iso*succino-*p*-toluidate, $C_{13}H_{17}O_3N$ (compare Comanducci and Lobello, Abstr., 1905, i, 271), forms large, colourless, tabular crystals, which belong to the monoclinic system [$a:b:c = 3{\cdot}4327:1:1{\cdot}4716$; $\beta = 68°49'$]. R. V. S.

Tetra- and Penta-methyl Orcinol. JOSEF HERZIG and FRANZ WENZEL [with KARL ZEIDLER] (*Monatsh.*, 1911, 31, 461—489).—Tetramethylorcinol, obtained on methylating orcinol in the nucleus, has been characterised by means of a dibromo-derivative, which is decomposed by dilute alkali hydroxide into fumaric acid and di*iso*propyl ketone.

In addition, a pentamethylorcinol is formed during methylation and characterised by a monobromo-derivative; it probably has the annexed formula. Tetramethylorcinol cannot be further methylated by methyl iodide and potassium hydroxide, and it is not therefore an intermediate product in the formation of pentamethylorcinol.



The yield of tetra- and penta-methylorcinol is unsatisfactory when working in methyl- or ethyl-alcoholic alkali hydroxide solution, and it appears to be more satisfactory in aqueous solution, where, however, pentamethylorcinol preponderates (compare Herzig and Erthal, following abstract).

* and *Ber.*, 1911, 44, 2362—2369.

Pentamethylorcinol has m. p. 8°, b. p. 120°/12 mm.

Dibromotetramethylorcinol separates in measurable monoclinic crystals, m. p. 79·5° [$a:b:c=0·7243:1:0·9614$; $\beta=96°18'$]. It is readily decomposed on heating with very dilute potassium hydroxide into di*iso*propyl ketone, fumaric acid, and a saturated monobasic *acid*, $C_{11}H_{16}O_4$, m. p. 165°. With diazomethane a *methyl* ester is formed, m. p. 64—67°, which yields the original substance on hydrolysis. The acid is not decomposed by concentrated potassium hydroxide, and 30% hydrogen peroxide solution is without action. The acid is therefore regarded as a substituted cyclic complex.

[With A. SCHWADRON.]—*Monobromopentamethylorcinol*, after purification by distillation in a vacuum, was obtained in transparent, monoclinic plates [$a:b:c=1·4653:1:0·7528$; $\beta=91°3'$], m. p. 43—45°. It is decomposed by dilute alkali hydroxide, yielding chiefly a neutral *oil*, $C_{12}H_{18}O_3$, insoluble in alkali hydroxide, b. p. 117°/16 mm., 225—229°/760 mm. It is attempted to explain these decompositions by regarding the bromo-compounds as derivatives of norcarane, in which the *cyclo*propane ring undergoes rupture. E. F. A.

Alkylation in the Nucleus. JOSEF HERZIG and BR. ERTHAL (*Monatsh.*, 1911, 32, 491—504. Compare Abstr., 1910, i, 667).—Tetramethylphloroglucinol when treated with methyl iodide and aqueous potassium hydroxide yields a mixture of hexa- and penta-methylphloroglucinol. Tetraethylphloroglucinol, however, when treated in the same way gives the methyl ether of tetraethylphloroglucinol, m. p. 69—71°, which is characterised by its resistance to alkaline hydrolysis. Phloroglucinol dimethyl ether under similar conditions chiefly yielded the trimethyl ether.

On methylation of orcinol in aqueous alkali, a mixture of tetra- and penta-methyl orcinol is obtained, but the tetramethyl derivative is not converted into the pentamethyl derivative in this manner.

With resorcinol the main product is a methyl ether of trimethylresorcinol, b. p. 102—106°/12 mm. Quinol yields the dimethyl ether.

From phloroglucinol, aqueous potassium hydroxide, and ethyl iodide, the *ethyl ether* of *pentaethylphloroglucinol*, an oil, b. p. 178—181°/15 mm., is obtained.

Silver phloroglucinolcarboxylate and ethyl iodide interact to yield almost entirely ethyl phloroglucinolcarboxylate, m. p. 123°. The amount of secondary action is very small; no product alkylated in the nucleus could be obtained, and the ester could be purified without difficulty. With methyl iodide secondary action takes place, and a product methylated in the ring is obtained.

Phloroglucinol and orcinol when methylated with methyl sulphate form a preponderating quantity of oxygen ethers, and homologues methylated in the nucleus could not be obtained.

Ethyl phloroglucinoldicarboxylate is quantitatively and without difficulty converted by diazomethane into the trimethyl ether, m. p. 88—91°.

Diazomethane is without action on ethyl succinylsuccinate.

E. F. A

Hexa- and Penta-methylphloroglucinol. JOSEF HERZIG and BR. ERTHAL (*Monatsh.*, 1911, **32**, 505—508. Compare Abstr., 1910, i, 607).—Hexamethylphloroglucinol does not react with *p*-nitrophenylhydrazine, semicarbazide, or amyl nitrite; it could not be reduced. It reacts with magnesium methyl iodide, forming a *compound*, $C_{15}H_{30}O_3$, m. p. 258—260°, which does not contain a methoxyl group, and is resistant towards the usual reagents.

Magnesium methyl iodide reacts with the methyl ether of pentamethylphloroglucinol, forming a *substance*, $C_{13}H_{22}O_2$, m. p. 67—68°, which likewise contains no methoxyl group. E. F. A.

Two Methods of Obtaining *cyclo*Butanol. Certain Transformations of *cyclo*Butanol Accompanied by Isomerisation. NICOLAUS J. DEMJANOFF and M. N. DOJARENKO (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 835—846).—It has been shown by Demjanoff (Abstr., 1908, i, 85) and by Zelinsky and Gutt (Abstr., 1908, i, 14) that the *cyclo*butanol obtained by Perkin (Trans., 1894, **65**, 950) by the action of nitrous acid on *cyclo*butylamine contains an admixture of *cyclo*propylcarbinol. The alcohol obtained by Dalle (Abstr., 1902, i, 525) by the action of nitrous acid on *cyclo*propylmethylamine is also a mixture of *cyclo*propylcarbinol and *cyclo*butanol. In order to prepare pure *cyclo*butanol, the authors have, therefore, had recourse to Simonini's method (Abstr., 1893, i, 391), and to the electrolysis of a solution of potassium *cyclo*butanecarboxylate containing potassium carbonate and potassium hydrogen carbonate (compare Hofer and Moest, Abstr., 1902, i, 736). The principal result of the experiments described below is that the ring of *cyclo*butanol is unstable towards acid reagents, and gives rise to compounds containing a *cyclo*propane ring.

cyclo*Butyl* cyclo*butanecarboxylate*,

$$CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CH\cdot CO_2\cdot CH<\begin{matrix}CH_2\\CH_2\end{matrix}>CH_2,$$

obtained in a 34·5% yield by the interaction of dry iodine and silver *cyclo*butanecarboxylate ($2C_4H_7\cdot CO_2Ag + I_2 = C_4H_7\cdot CO_2\cdot C_4H_7 + CO_2 + 2AgI$), is a liquid, b. p. 198·5—199°/750 mm., D_{15}^{15} 1·003, $D_{18\cdot9}^{18\cdot9}$ 1·007, D_{23}^{23} 0·9980, $n_D^{18\cdot9}$ 1·4551. Hydrolysis of this ester yields *cyclo*butanecarboxylic acid and *cyclo*butanol, b. p. 123°/733 mm., D_{15}^{15} 0·9226, $D_{18\cdot9}^{18\cdot9}$ 0·9206, D_{25}^{25} 0·9181, $n_D^{18\cdot9}$ 1·4339. On oxidation with nitric acid, it yields succinic acid, which is formed only in comparatively small quantity from *cyclo*propylcarbinol under similar conditions.

*cyclo*Butanol and *cyclo*butyl *cyclo*butanecarboxylate are also obtained as the products of hydrolysis of potassium *cyclo*butanecarboxylate.

Oxidation of *cyclo*butanol with chromic oxide and sulphuric acid gives, not *cyclo*butanone, but the isomeric *cyclo*propanealdehyde (compare Abstr., 1908, i, 156).

In spite of small differences in the b. p. and sp. gr., the acid obtained by converting *cyclo*butanol into the bromo-derivative and treating the magnesium compound of the latter with carbon dioxide (*ibid.*) bears a decided resemblance to allylacetic acid. T. H. P.

***p*-Hydroxybenzyl-methylamine and -dimethylamine.** MARC TIFFENEAU (*Bull. Soc. chim.*, 1911, [iv], **9**, 825—828).—p-*Hydroxy*-

benzylmethylamine, $HO\cdot C_6H_4\cdot CH_2\cdot NHMe$, is obtained as the *hydriodide*, m. p. 149—150° (approx.), by the action of hydriodic acid on p-*methoxybenzylmethylamine*, $MeO\cdot C_6H_4\cdot CH_2\cdot NHMe$, D_0^0 1·025, b. p. 121°/14 mm. (*hydrochloride*, m. p. 166°), itself formed by the interaction of anisyl chloride, D_0^0 1·072, b. p. 116—120°/15 mm., or bromide, D_{19}^{19} 1·395, b. p. 129°/6 mm. (approx.), and methylamine in alcohol in a closed tube. Some *di*-p-*methoxybenzylmethylamine*, D_0^0 1·0794, b. p. 210°/15 mm., is also formed in this reaction. On demethylation, it gives *di*-p-*hydroxybenzylmethylamine*, $NMe(CH_2\cdot C_6H_4\cdot OH)_2$, the *hydrochloride* of which has m. p. 197—199°.

p-*Hydroxybenzyldimethylamine*, $HO\cdot C_6H_4\cdot CH_2\cdot NMe_2$, m. p. 112°, reduces ammoniacal silver nitrate, Millon's reagent, or iodic acid, but does not give any coloration with ferric chloride; the *hydrochloride*, m. p. 194°, and the *hydriodide*, m. p. 135°, are both crystalline. It is produced in a manner analogous to its lower homologue by demethylating p-*methoxybenzyldimethylamine*, D_0^0 0·9878, D_{15}^{15} 0·976, b. p. 110—111°/16 mm., which furnishes a *hydrochloride*, m. p. 157°, *hydriodide*, m. p. 145°, and *methiodide*, m. p. 158°. The last-mentioned substance on demethylation by hydriodic acid furnishes p-*hydroxybenzyltrimethylammonium iodide*, $HO\cdot C_6H_4\cdot CH_2\cdot NMe_3I$, m. p. 191°, which is readily transformed by silver chloride into the corresponding *chloride*, m. p. 98°.

p-Methoxybenzyldimethylamine is converted by acetic anhydride into anisyl alcohol and dimethylacetamide, and the demethylated base is similarly transformed by this reagent. T. A. H.

3 : 4 : 5-Trinitroveratrole. ALFONS KLEMENC (*Monatsh.*, 1911, **32**, 457—459).—3 : 4 : 5-Trinitroveratrole, m. p. 144—145°, has been described by Tiemann and Matsmoto (this Journ., 1876, ii, 524) and by Blanksma (Abstr., 1905, i, 277).

It is now obtained on nitrating hemipinic acid with fuming nitric acid without a solvent and also by heating 5 : 6-dinitro-2 : 3-dimethoxybenzoic acid with fuming nitric acid, a method of preparation which establishes its constitution. E. F. A.

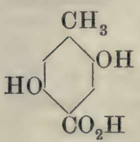
Dehydration of the Glycols of Anethole and *iso*Safrole. VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 940—946).—The author dissociates himself from the attack (Abstr., 1908, i, 901) of his former collaborator Balbiano (compare Balbiano and Paolini, Abstr., 1906, i, 186) on the statements of Tiffeneau and Daufresne (Abstr., 1907, i, 701), and confirms the statements of these authors. R. V. S.

Action of Bromine in Presence of Aluminium Bromide on *cyclo*Hexanol and *cyclo*Hexanone. FERNAND BODROUX and FELIX TABOURY (*Compt. rend.*, 1911, **153**, 349—350).—Hexabromobenzene is formed when *cyclo*hexanol is dropped into excess of bromine containing 1% of aluminium in solution. *cyclo*Hexanone on treatment in the same way forms a *tetrabromo*-derivative crystallising in prisms, m. p. 117° (decomp.). When this is heated at 120—125°, it loses bromine

and hydrogen bromide, and becomes converted into a liquid having the properties of a bromophenol. Small quantities of uninvestigated substances of high melting point are also formed in this bromination.

W. O. W.

Position of the Substituents in Hydroxyhomosalicylic [Dihydroxytoluic] Acid. HANS SCHMID (*Monatsh.*, 1911, 32, 435—445).—*Toluquinol monoacetate* crystallises in long, lustrous needles, m. p. 92°. The *diacetate* forms granular crystals, m. p. 49°; on oxidation in neutral solution with potassium permanganate, gentisic acid is obtained.



Dihydroxytoluic acid, prepared by heating toluquinol with potassium hydrogen carbonate and glycerol, forms a *diacetate*, m. p. 129°. This on oxidation with permanganate is converted into 2:5-dihydroxyterephthalic acid. Accordingly, dihydroxytoluic acid (hydroxyhomosalicylic acid) is represented by the annexed formula.

E. F. A.

***p*-Hydroxyphenylglyoxylic, *p*-Hydroxyphenylacetic, and *p*-Hydroxyphenylglycollic [*p*-Hydroxymandelic] Acids.** JULES ALOY and CH. RABAUT (*Bull. Soc. chim.*, 1911, [iv], 9, 762—764).—By the oxidation of *p*-acetylaminoacetophenone by alkaline permanganate there results p-*acetylaminophenylglyoxylic acid*,

$$NHAc\cdot C_6H_4\cdot CO\cdot CO_2H,$$

pale yellow crystals, m. p. 186—187°, which yields a white, crystalline *silver* salt, and a yellow *phenylhydrazone*, m. p. 200—202° (decomp.). This acid on hydrolysis and subsequent diazotisation yields *p*-hydroxyphenylglyoxylic acid (Abstr., 1899, i, 288, 437). From the latter acid by reduction with hydriodic acid, *p*-hydroxyphenylacetic acid is formed.

p-Hydroxymandelic acid can be obtained from the corresponding glyoxylic acid by the action of sodium amalgam (compare Ellinger and Kotake, Abstr., 1910, i, 384).

W. G.

Theoretical Considerations on the Isomerism in Ethylene Derivatives. EMIL ERLENMEYER (*Biochem. Zeitsch.*, 1911, 35, 149—165).—Substances of the general formula $C(R^1R^2R^3)\cdot C(R^4R^5R^6)$ have been obtained in four modifications. If, however, the models representing these modifications, which are due to relative differences of position of the groups attached to each carbon atom, be twisted about the axis, then, according to van't Hoff, twelve modifications should exist. The author gives reasons for assuming that such do in reality exist, although they have not been definitely isolated. These are (1) the results obtained in the determination of the crystallographic and optical properties of the storax-cinnamic acids; (2) the fact that equimolecular quantities of phenyl-lactic acid and cinnamic acid are obtained by the reduction of phenylbromolactic acid and other similar reactions; (3) the existence of different malic acids, as demonstrated by Mayer and Aberson; (4) the fact that, according to Walden, *l*-chlorosuccinic acid yields on treatment with potassium hydroxide the

d-malic acid, whereas by treatment with silver hydroxide the *l*-variety is obtained. If, in the case of ethylene compounds, the double bond between two multivalent elements be represented in the model in a similar manner to the bond between two groups, so as to form an angle, then, by the application of the above-mentioned conceptions as to the rotation of the model in the case of compounds of the $C(R^1R^2R^3)\cdot C(R^4R^5R^6)$ type, a whole series of isomeric derivatives with the ethylene linking should exist. This theory of the author is illustrated by his results with cinnamic acid, and numerous diagrams of the models are given in the paper. S. B. S.

The Possibility of the Existence of Molecular Asymmetric Storax-Cinnamic Acids. EMIL ERLENMEYER and G. HILGENDORFF (*Biochem. Zeitsch.*, 1911, 35, 134—148).—Storax-cinnamic acid was converted into the dibromo-derivative, and this substance, by distillation with steam, into *dl*-phenylbromolactic acid. The latter was separated into its antipodes by means of the cinchonine salts. The *d*- and *l*-bromo-acids were then converted by means of sodium amalgam into the corresponding *d*- and *l*-phenyl-β-lactic acids, which, on treatment with hydrochloric acid at 46°, lose water and are converted into cinnamic acid. In only one case were the cinnamic acids thus obtained from optically active lactic acids themselves directly optically active. As, however, it is probable that optically active cinnamic acids, if they exist, have only a small rotation, it was possible that the amounts of such acids were too small in these preparations to affect the activity. They were therefore converted into the dibromides, and these substances into the sodium salts of the corresponding oxidoacrylates, as the authors have shown that the substances, if optically active, have a large rotation. It was found that the oxidoacrylates prepared from cinnamic acids which were obtained from optically active phenyllactic acids were active, the rotation corresponding in direction with that of the lactic acid from which they were obtained. Furthermore, a few of the crystals of the cinnamic acids obtained from optically active lactic acids showed asymmetric structure, whereas the crystals of storax-cinnamic acid itself were symmetrical.

Attempts were also made to prepare active cinnamic acids by the direct reduction of the active phenylbromolactic acids by means of zinc and alcohol, and it was found that this reaction yielded equal molecules of cinnamic acids and phenyl-β-lactic acids. The changes in the rotation during the reaction were also followed, and it was found that at the end of the reduction very little, if any, changes in the rotation had taken place. As the solution had a considerably higher rotation than could be accounted for by the phenyl-lactic acids they contained, the conclusion was drawn that the zinc salts of the cinnamic acids in the solution were active. On attempting to prepare the free acids from the zinc salts, the authors did not succeed in obtaining optically active acids, although they have obtained preparations from the optically active lactic acids showing distinct traces of asymmetry. They conclude that optically active cinnamic acids exist which are very readily racemised. S. B. S.

The Isomeric Acids of the Cinnamic Acid Series. EMIL ERLENMEYER (*Biochem. Zeitsch.*, 1911, 34, 355—386).—The differences between the natural storax-cinnamic acid and the synthetic acid obtained from benzaldehyde from various sources are summarised, and the crystalline measurements of the dibromides and dichlorides are given. It is concluded that the synthetic acid is a mixture of the storax acid with heterocinnamic acid; the properties of these latter acids are contrasted, and the crystalline measurements of the dibromides are given. The separation of the two acids present in the synthetic acid can be accomplished (1) by the fractional distillation of the ester; (2) by the incomplete addition of hypochlorous acid, the residue of unacted on acid consisting of the hetero-β-acid; (3) by the fractional precipitation of the acid from a solution of the sodium salt. The evidence is then summarised, which tends to show that the various cinnamic acids are isomerides with the same chemical constitution. (*a*) The evidence is summarised tending to show that the differences are not due to accidental impurities. (*b*) The acids can be converted into dibromides, from which, by various reactions, the original acids can be regenerated in unchanged form. Eight such series of reactions are mentioned. (*c*) It is shown that benzaldehydes of different origin yield different cinnamic acids, those aldehydes containing hydrocyanic acid yielding storax-cinnamic acid, whereas the aldehydes which have been completely separated from hydrocyanic acid yield the synthetic (mixed acids) cinnamic acid. The differences depend therefore on the grouping contained in the benzaldehyde. (*d*) Evidence is summarised to show that the differences are not due to impurities in the aldehyde. (*e*) Finally, evidence is brought forward to show that in the process by removal of the hydrocyanic acid from the natural aldehydes in which calcium hydroxide is used, the aldehyde undergoes isomeric change, due to the presence of alkali. Furthermore, if storax-cinnamic acid be oxidised to benzaldehyde, care being taken to prevent the mixture from becoming alkaline, an aldehyde is obtained from which, by Perkin's synthesis, the original acid can be regenerated. If, however, the oxidation of the acid to benzaldehyde be carried out in alkaline solution, an aldehyde is obtained from which, by the Perkin synthesis, instead of storax-cinnamic acid, a mixture of this and the hetero-β-acid (synthetic cinnamic acid) is obtained.

S. B. S.

The Behaviour of Certain Mixtures of Storax Cinnamic Acid with Certain Substituted Cinnamic Acids. EMIL ERLENMEYER and G. HILGENDORFF (*Biochem. Zeitsch.*, 1911, 34, 405—416).—To ascertain definitely whether the synthetic acid differs from the storax acid, owing to the presence of certain impurities, the properties of the mixture of this acid with substituted cinnamic acids (chloro-, hydroxy-, methoxy-, and methyl derivatives) were investigated. Experiments on the separation of *p*-methylcinnamic acid from cinnamic acid were carried out. Crystallographic measurements of the mixtures were also made. The results confirm the statement in a previous paper, that the synthetic acid is not a mixture of cinnamic with a substituted cinnamic acid.

S. B. S.

Further Experiments on the Separation of Heterocinnamic Acid. EMIL ERLENMEYER and G. HILGENDORFF (*Biochem. Zeitsch.*, 1911, **34**, 417—427).—A series of experiments on the fractional precipitation of the synthetic cinnamic acid from the solution of the sodium salt by acid are described, which were undertaken with the object of determining whether the hetero-acid could be further separated into other constituents. As no acid other than the hetero-acid could be isolated by this method, the conclusion is drawn that this is the only acid accompanying the storax-cinnamic acid present in the synthetic product. S. B. S.

Action of Anisaldehyde and Piperonaldehyde on the Sodium Derivative of Phenylacetonitrile. FERNAND BODROUX (*Compt. rend.*, 1911, **153**, 350—351).—Anisaldehyde and piperonaldehyde react with the sodium derivative of phenylacetonitrile, forming the unsaturated nitriles, α-phenyl-*p*-methoxycinnamonitrile (Frost, Abstr., 1889, 597) and α-phenyl-3 : 4-methylenedioxycinnamonitrile (Walther and Wetzlich, Abstr., 1900, i, 438) respectively. On hydrolysis these substances yield *α-phenyl-*p*-methoxycinnamic acid*, $OMe\cdot C_6H_4\cdot CH{:}CPh\cdot CO_2H$, needles, m. p. 188°, and *α-phenyl-3 : 4-methylenedioxycinnamic acid*,

$$CH_2{:}O_2{:}C_6H_3\cdot CH{:}CPh\cdot CO_2H,$$

needles, m. p. 233°. W. O. W.

Interchange of Primary, Secondary, and Tertiary Alkyl Groups in the Esters of Organic Acids. MICHAEL PFANNL (*Monatsh.*, 1911, **32**, 509—522. Compare Abstr., 1910, i, 480; also Kommenos, Abstr., 1910, i, 361).—The experiments were made to establish the interchange of secondary and tertiary alcohols with primary, and to show the influence of the nature and structure of the alkyl group on the reaction velocity. The esters of terephthalic acid were allowed to react with methyl alcohol in proportions, so that the equivalent of 0·5 gram of dimethyl terephthalate was present in 10 c.c. of methyl alcohol. Under these conditions about 20% of change is indicated by the crystallisation of the dimethyl ester.

Under similar conditions the diethyl ester required 1 min. 40 sec. for 20% conversion into dimethyl ester, the di-*n*-propyl ester required 3 min. 50 sec., the di-*n*-butyl ester 3 min. 30 sec., the di*iso*butyl ester 5 min. 40 sec., the di*iso*propyl ester 14 min. 10 sec., whilst the di-*tert.*-butyl ester did not react within forty-eight hours. It is obvious that retardation is caused by the branching of the chain, particularly by the secondary and tertiary character of the alkyl.

Whereas methyl is interchanged with the *sec.*-*iso*propyl group in the esters of terephthalic acid at the ordinary temperature and with very little alkali, the *tert.*-butyl group can only be introduced by using much alkali and heating.

tert.-Butyl benzoate, obtained in this manner from methyl benzoate and *tert.*-butyl alcohol, is a highly refractive, oily liquid, very similar to other esters of benzoic acid; it has b. p. 94°/10 mm., 213°/760 mm., decomposing to benzoic acid when distilled.

Di-*n*-butyl terephthalate forms long, colourless needles, m. p. 16°.

Di-tert.-*butyl terephthalate* crystallises in stout, lustrous prisms, m. p. 118°; it is obtained by fractional distillation of the product obtained by heating the dimethyl ester with *tert.*-butyl alcohol and excess of alkali hydroxide. E. F. A.

Friedel-Crafts' Reaction. OTTOKAR HALLA (*Monatsh.*, 1911, **32**, 637—640).—On heating xanthone with the equivalent quantity of phthalic anhydride, dissolved in benzene containing a little toluene, and aluminium chloride, no interaction with the xanthone was found to take place, but the reaction mixture contained benzoylbenzoic and toluoylbenzoic acids.

Experiments made with varying proportions of toluene showed that when phthalic anhydride, in equivalent quantity to the toluene taken, was used in every case, toluoylbenzoic acid was the sole product.

It was supposed that benzoylbenzoic acid was first formed, and the benzoyl group subsequently displaced by toluoyl, as Heller and Schülke (Abstr., 1908, i, 994) supposed in the case of naphthoylbenzoic acid. This displacement is proved, however, not to take place on heating benzoylbenzoic acid with toluene and aluminium chloride. The change is attributed to the ready substitution of the alkylated benzene nucleus. E. F. A.

Glycocholic Acid and Para-glycocholic Acid. EUGEN LETSCHE (*Zeitsch. physiol. Chem.*, 1911, **73**, 308—311. Compare Abstr., 1909, i, 587).—Glycocholic acid crystallises with $1\frac{1}{2}H_2O$; it sinters at 126°, m. p. 130°. The anhydrous acid sinters at 130—132°, decomp. 154—155°. When heated at 100° in aqueous suspension for some hours, para-glycocholic acid is formed; it crystallises with $1H_2O$, sinters at 186°, decomp. 198°, or when anhydrous it sinters at 193°, decomp. 198°. The two acids are regarded as isomerides. E. F. A.

Separation and Transformation of the Benzaldehydes. EMIL ERLENMEYER, G. HILGENDORFF, and TH. MARX (*Biochem. Zeitsch.*, 1911, **34**, 386—404).—The attempts made to separate the benzaldehydes from mixtures are described. Fractional distillation led to no satisfactory results. A partial separation could, however, be effected by fractional condensation with sodium acetate and acetic anhydride, or by fractional addition of hydrocyanic acid; owing to the fact that the isomerides possess different velocity fractions in these cases. Experiments are also described to show how the "natural" benzaldehyde can be converted into the "synthetic" benzaldehyde by the action of alkaline reagents, or by heating with platinised abestos; attempts to convert the synthetic acid into the hetero- and storax-acids are also mentioned. S. B. S.

The Electrolytic Reduction of Anisaldehyde. JULIUS TAFEL and WILHELM SCHEPSS (*Ber.*, 1911, **44**, 2148—2154).—In accordance with the results obtained by Tafel (Abstr., 1909, i, 766) on the reduction of methyl *iso*-amyl ketone at cadmium cathodes, it was to be expected that the aldehyde group would undergo reduction to a greater extent at cathodes of this metal than at other cathodes. The authors

have, therefore, studied the electrolytic reduction of anisaldehyde in aqueous-alcoholic solution of sulphuric acid, investigating the influence of current density, temperature, and material of which the cathode was made, especially in so far as the yield of *p*-tolyl methyl ether, $C_6H_4Me\cdot OMe$, was concerned.

The complete reduction of the aldehyde group takes place to a much greater extent at cadmium electrodes than at electrodes of other metals. Under the conditions of current density and temperature given by Law (Trans., 1906, **89**, 1512, 1520; 1907, **91**, 748; 1911, **99**, 1113), a 37% yield of *p*-tolyl methyl ether was obtained, and the yield could be further increased to 60% by increasing the current density, the temperature not being allowed to rise above 25°. The formation of anisic alcohol takes place to a slight extent only, whereas Law (*loc. cit.*) found the opposite to be the case with copper electrodes.

In addition to *p*-tolyl methyl ether and anisic alcohol, some resin is always formed, together with a mixture of solid substances of high boiling point, which contains the isomeric hydroanisoins, dimethoxystilbene, and probably also dimethoxydibenzyl. The total quantity of these bimolecular products formed depends chiefly on the temperature, increasing very rapidly with rise in temperature. At 35°, however, the amount formed is independent of the strength of the current within fairly wide limits.

The formation of resin was always very small (0·5—7%), only becoming appreciable when very strong or too weak acid was used.

T. S. P.

Phenolic Aldehydes. I. Reactivity of the Aldehyde Group in Phenolic Aldehydes. Hermann Pauly and Richard (Freiherr) von Buttlar (*Annalen*, 1911, **383**, 230—288).—Attention has been called by several investigators to the fact that certain aromatic aldehydes do not behave normally in the Grignard reaction. Béhal and Tiffeneau, in particular, obtain very poor yields of the expected propenyl compounds from protocatechualdehyde, *p*-hydroxybenzaldehyde, vanillin and *iso*vanillin, and magnesium ethyl bromide, although the neutral ethers react normally (Abstr., 1908, i, 260).

[With Karl Lockemann.]—It is now found that salicylaldehyde and magnesium ethyl iodide give, in 92% yield, a mixture of o-*propenylphenol*, $OH\cdot C_6H_4\cdot CH:CHMe$, m. p. 34·8°, b. p. 229—231°, and a yellow oil, b. p. about 235°/23 mm., which is probably a bimolecular form of *o*-propenylphenol. So also, *o*-vanillin gives 46% of o-iso-*eugenol* (2-*hydroxy*-3-*methoxypropenylbenzene*),

$$OMe\cdot C_6H_3(OH)\cdot CH:CHMe,$$

m. p. 81° (*bromo*-o-iso-*eugenol dibromide*, $C_{10}H_{11}O_2Br_3$, m. p. 111°); 2-3-dimethoxybenzaldehyde yields 93% of 2:3-*dimethoxyphenylmethylcarbinol*, $C_6H_3(OMe)_2\cdot CHMe\cdot OH$, b. p. 151—152°/15 mm., D_4^{20} 1·1213 (*phenylurethane*, m. p. 127°), and 2:3-dihydroxybenzaldehyde yields 85% of a *substance*, which is probably a polymeride, $(C_9H_{10}O_2)_4$, of *o*-propenylcatechol.

The striking difference of behaviour of the preceding aldehydes in the Grignard reaction has induced the authors to examine the reactivity of phenolic aldehydes in other directions. Their conclusions

that mono- and di-hydric phenolic aldehydes and their acyl derivatives show, in contrast to their neutral ethers, abnormal behaviour in the following reactions, are based to a large extent on observations already recorded in the literature, and are most concisely represented by the table (*a* = smooth reaction or yield greater than 75%; *b* = fair reaction or yield about 60%; *c* = bad reaction or yield about 30%; *d* = very bad or no reaction).

	Ethers of phenolic aldehydes.	Hydroxy-benz-aldehydes.			Dihydroxy-benz-aldehydes.				Vanillins.			*cyclo*Carbonates of di-hydroxybenz-aldehydes.	
		o-	*m*-	*p*-	2:3,	2:4,	2:5,	3:4.	OH 2, OMe 3,	3, 4,	4. 3.	2:3	3:4.
Cannizzaro reaction	*a*	*d*		*d*		*d*	*d*	*d*			*d*		
Benzoin condensation	*a*	*d*											
Acetal formation (by alcohol and HCl).	*b*	*d*		*d*				*d*		*d*	*d*		*d*
Acetal formation [by $CH(OR)_3$]	*a*	*a*	*a*	*a*	*d*	*d*	*d*	*d*					*d*
Hydroxamic acid formation [by $NH(OH)_2$]	*a*	*c*	*a*	*d*				*d*		*a*	*d*		*d*
Grignard reaction...	*a*	*a*		*c*	*a*(?)			*d*	*a*(?)	*c*	*c*		*d*
Doebner's reaction ($CH_3\cdot CO\cdot CO_2H$ and $\beta C_{10}H_7\cdot NH_2$)	*a*	*a*	*a*	*b*	*d*	*d*	*d*	*b*	*a*	*a*	*b*		
Schiff's reaction (magenta and H_2SO_3)	*a*	*b*	*b*	*d*	*c*	*d*	*b*	*d*	*b*	*c*	*c*	*b*	*b*

The diminution in the reactivity of the aldehyde group does not always coincide with the entrance of the first hydroxyl group, but usually is quite evident when the second hydroxyl group is introduced, particularly in the para-position with respect to the aldehyde group.

Various causes of the abnormalities are suggested and discussed. The original paper must be consulted for a comprehension of the only satisfactory explanation, which is based on Stark's electro-atomistic theory of valency.

The following acetals have been obtained from methyl orthoformate by a modification of Claisen's process. p-*Hydroxybenzaldehyde dimethyl acetal*, $OH\cdot C_6H_4\cdot CH(OMe)_2$, m. p. 60—64°, m-*hydroxybenzaldehyde dimethyl acetal*, b. p. 150°/11 mm. (decomp.); o-*hydroxybenzaldehyde dimethyl acetal*, b. p. about 65°/0·4 mm. These acetals are extremely sensitive to the action of alkalis, and the first and the last, when heated, lose methyl alcohol and yield substances which are apparently mixtures of the hydroxybenzaldehyde and the quinomethyl ether, $O:C_6H_4:CH\cdot OMe$. The following mercaptals are described: m-*Hydroxybenzaldehyde dimethyl mercaptal*, $OH\cdot C_6H_4\cdot CH(SMe)_2$, very viscous oil; p-*hydroxybenzaldehyde dimethyl mercaptal*, m. p. 73·5°; *protocatechualdehyde dimethyl mercaptal*, m. p. 108—109°; o-*protocatechualdehyde di*-p-*nitrobenzyl mercaptal*, $C_6H_3(OH)_2\cdot CH(S\cdot CH_2\cdot C_6H_4\cdot NO_2)_2$, m. p. 177°, yellow prisms; *gentisinaldehyde di*-p-*nitrobenzyl mercaptal*, m. p. 170°, green prisms. The following colours and m. p.'s refer to the substituted β-naphthacinchonic acids obtained by Doebner's method from the corresponding aldehydes: m-*hydroxyphenyl*-, yellow powder,

284·5°; p-*hydroxyphenyl-*, pale yellow powder, 325·5°; m-*hydroxy*-p-*methoxyphenyl-*, citron-yellow powder, 295°; o-*hydroxy*-m-*methoxyphenyl-*, white powder, 251°; mp-*dihydroxyphenyl-β-naphthacinchonic acid*, orange-yellow powder, 317·5°. C. S.

Phenolic Aldehydes. II. Reactivity of the Phenolic Group in Phenolic Aldehydes. HERMANN PAULY, KONRAD SCHÜBEL, and KARL LOCKEMANN (*Annalen*, 1911, **383**, 288—337. Compare preceding abstract).—The acid character of a phenol is enormously increased by the entrance of an aldehyde group into the nucleus. By titration with phenolphthalein as indicator, 2 : 3-, 2 : 4-, and 2 : 5-dihydroxybenzaldehydes behave as monobasic acids, as do also protocatechualdehyde, vanillin, and *o*- and *p*-hydroxybenzaldehydes. The acidifying influence of the aldehyde group, therefore, is exerted on the hydroxyl group in any position in the nucleus, but it is least in the meta-position, and apparently is exerted only on one hydroxyl group, conductivity measurements showing that the k values of *p*-hydroxybenzaldehyde and protocatechualdehyde are $2·2 \times 10^{-8}$ and $2·8 \times 10^{-8}$ respectively at 25° (for phenol, k $1·3 \times 10^{-10}$ at 18°). Corresponding with the increased mobility (that is, the weakening of the union between the hydrogen and the oxygen atoms) of the hydrogen atom of the hydroxyl group in the para-position in protocatechualdehyde (as compared with the mobility of the hydrogen atom in phenol or catechol), experiment shows that a similar loosening is to be observed in the derivatives of the phenols; thus the *cyclo*carbonate of protocatechualdehyde, by treatment with water, evolves carbon dioxide about seventy-five times as rapidly as the *cyclo*carbonate of catechol. (This ratio is approximately the ratio of the k values of protocatechualdehyde and catechol [compare Rivett and Sidgwick, Trans., 1910, **97**, 1677]). Moreover, this loosening of the linking at the oxygen atom in the para-position (or in the ortho-position in the case of derivatives of 2 : 3-dihydroxybenzaldehyde) is seen in the following instances. Protocatechualdehyde *cyclo*carbonate is converted by boiling methyl alcohol into the *m*-methyl carbonate,

$$CHO·C_6H_3(OH)·O·CO_2Me,$$

m. p. 96° (formerly given as 93°), the orientation of which is proved by methylation and subsequent hydrolysis, whereby *iso*vanillin is obtained. Similarly, the *cyclo*carbonate of *o*-protocatechualdehyde is converted into *methyl* o-*protocatechualdehyde*-m-*carbonate*,

$$CHO·C_6H_3(OH)·O·CO_2Me,$$

m. p. 115°, the orientation of the hydroxyl and aldehyde groups being shown by the exact analogy of the substance to salicylaldehyde. Again, protocatechualdehyde *cyclo*carbonate is converted by piperidine into *protocatechualdehyde*-m-*carbopiperidide*,

$$CHO·C_6H_3(OH)·O·CO·C_5NH_{10},$$

m. p. 123° (*phenylhydrazone*, $C_{19}H_{21}O_3N_3$, m. p. 159°), which yields *iso*vanillin by methylation and subsequent hydrolysis. Finally, phenylhydrazine acts on the *cyclo*carbonate to form, first, the *phenylhydrazone*, $CO_3{:}C_6H_3·CH{:}N·NHPh$, m. p. 177°, and then the *phenylhydrazonecarbophenylhydrazide*, $NHPh·N{:}CH·C_6H_3(OH)·O·CO·NH·NHPh$, m. p. 186°.

The salts of phenolic aldehydes with the alkali metals and metals of the alkaline earths are frequently strongly coloured. The authors do not commit themselves by giving a quinonoid constitution to these salts; in fact, they are inclined against this view on account of the persistence of the colour in the presence of even fairly strong reducing agents.

o-Protocatechualdehyde (2 : 3-dihydroxybenzaldehyde) forms an *anil*, $C_6H_3(OH)_2\cdot CH\colon NPh$, scarlet needles, m. p. 135°; *β*-naphthylamine derivative, $C_6H_3(OH)_2\cdot CH\colon N\cdot C_{10}H_7$, bluish-red needles, m. p. 164°; phenylhydrazone, m. p. 167° (not 176° as given previously); *semicarbazone*, m. p. 226° (corr., decomp.), and orange-yellow *barium* salt, $C_7H_4O_3Ba,4H_2O$, which loses $2H_2O$ at 105° and another $2H_2O$ at 170—180°. The 3-*methyl ether*-2-*methyl carbonate*,

$$OCH\cdot C_6H_3(OMe)\cdot O\cdot CO_2Me,$$

m. p. 60°, is obtained from the potassium salt of *o*-vanillin and methyl chlorocarbonate in benzene.

Protocatechualdehyde forms a yellow *barium* salt, $C_7H_4O_3Ba,2H_2O$, which loses one or two molecules of water at 160—170° according to the duration of the heating, and an almost colourless *barium hydrogen* salt, $(C_7H_5O_3)_2Ba,3H_2O$. When the barium salt is heated with methyl sulphate (rather more than 1 mol.) in benzene, vanillin and *iso*vanillin are obtained in equal amount, but when protocatechualdehyde is heated with alcoholic potassium hydroxide (rather more than 1 mol.) and methyl iodide, the ratio of *iso*vanillin to vanillin is 9 : 1.

Vanillin methyl 4-*carbonate*, $CHO\cdot C_6H_3(OMe)\cdot O\cdot CO_2Me$, m. p. 91·5°, is obtained by heating vanillin and methyl-alcoholic potassium hydroxide with methyl chlorocarbonate. iso*Vanillin methyl* 3-*carbonate*, m. p. 121°, is prepared by heating the sodium salt of *iso*vanillin and methyl chlorocarbonate in benzene.

Protocatechualdehyde *cyclo*carbonate forms a *semicarbazone*,

$$CO_3\colon C_6H_3\cdot CH\colon N\cdot NH\cdot CO\cdot NH_2,$$

m. p. 220° (decomp.), and reacts with methyl mercaptan in the presence of hydrogen chloride only at the aldehyde group (compare behaviour with methyl alcohol), forming the *dimethyl mercaptal*, $CO_3\colon C_6H_3\cdot CH(SMe)_2$, m. p. 56·5°.

Salicylaldehyde and piperidine (2 mols.) react to form the *dipiperidil*, $OH\cdot C_6H_4\cdot CH(NC_5H_{10})_2$, m. p. 87—88°, colourless plates. Gentisinaldehyde forms a *semicarbazone*, $C_6H_3(OH)_2\cdot CH\colon N\cdot NH\cdot CO\cdot NH_2$, m. p. 249°. An attempt to form an *aci*-ether of salicylaldehyde has not given a conclusive result. C. S.

Theory of the Phenomena of Halochromy. II. Paul Pfeiffer [and, in part, B. Friedmann, Z. Goldberg, E. Pros, and V. Schwarzkopf] (*Annalen*, 1911, 383, 92—155. Compare Abstr., 1910, i, 852).—The author's theory of halochromy is based on the conception that the molecule of the metallic salt or acid (termed the addendum for brevity) unites as a whole co-ordinatively at the carbonyl oxygen atom, thereby neutralising its free affinity, and consequently increasing the free affinity of the carbonyl carbon atom, which thus becomes more unsaturated and acquires the character of a chromophore; the

phenomenon of halochromy is ascribed to the presence of such unsaturated carbon atoms.

The halochromatic substances previously described (*loc. cit.*) containing tin tetrahalides as addenda, are almost invariably composed of 2 mols. of the carbonyl compound and 1 mol. of the tin tetrahalide, are represented by the constitution $X_4Sn\langle{}^{O:CRR'}_{O:CRR'}$, and are colourless, or nearly so, on account of the relatively simple constitution of the organic component. The substances now described contain aromatic carbonyl compounds, and are usually highly coloured; they are still composed of 2 mols. of the carbonyl compound and 1 mol. of the tin tetrahalide, and therefore receive the constitution given above. Since this constitution is general for halochromatic substances containing a tin tetrahalide, it probably holds for substances containing other addenda.

The colour, but not the composition, of halochromatic substances of the type $X_4Sn\langle{}^{O:CRR'}_{O:CRR'}$ (where R and R′ are either or both aromatic) is influenced by the presence of chromophores in R and R′.

The influence of auxochromic groups in R and R′ is interesting. The organic components are the isomeric hydroxybenzaldehydes, methoxybenzaldehydes, and the hydroxyacetophenones, the addendum being a tin tetrahalide, an acid, or an alkali. The presence of the auxochrome intensifies the colour of the halochromatic substance, its influence being greatest when it is ortho to the carbonyl group and least in the para-position; however, when an ethenoid group is present between the aromatic nucleus and the carbonyl group (for example, the isomeric hydroxy- or methoxy-cinnamic acids), the influence of the auxochrome on the colour of the halochromatic substance is normal, being greatest in the ortho- and least in the meta-position. When the hydroxyl group is acetylated, colour disappears; thus *acetylsalicylaldehyde tin tetrachloride* is an unstable, greyish-white, crystalline substance, and has the constitution

$$Cl_4Sn\langle{}^{O:CH\text{——}}_{O:CMe\cdot O}\rangle C_6H_4.$$

The dependence of halochromy on the functional nature of the carbonyl compound is illustrated by comparing the halochromy of a series of additive compounds obtained from carbonyl compounds R·CO·A (where A is a hydrogen atom or an alkyl, hydroxy-, alkyloxy-, or amino-group) and an addendum which is either (i) concentrated sulphuric acid, (ii) hydrogen chloride in alcohol or glacial acetic acid, (iii) aqueous potassium hydroxide, (iv) aqueous ammonia, or (v) tin tetrachloride. When R·CO· is a benzoyl, hydroxybenzoyl, or cinnamoyl group, pronounced halochromy is observed only when the addendum is (i) and A is a hydrogen atom or an alkyl group. The explanation of this behaviour is as follows. Evidently the degree of unsaturation of the carbonyl carbon atom (which is essentially the cause of halochromy) must be influenced by the nature of R and A. When these are able to neutralise a portion of the free affinity of the carbonyl carbon atom (as, for example, when A is OH, OR′, NH_2, NR'_2, etc.), its chromophoric character is weakened, and the additive com-

pounds will be colourless or less coloured than those in which A is a hydrogen atom or an alkyl group. (In this connexion it is instructive to contrast the absence of selective absorption in oxalic acid, ethyl oxylate, and oxamide with the yellow colour of glyoxal and of dimethyl diketone.)

The influence of the addendum on halochromy can be ascertained by comparing a series of additive compounds, X···O:CRR′, containing different X's. The author's theory requires that the colour should be more intense the stronger the attachment of the addendum to the carbonyl oxygen atom. There is no doubt that such attachment is exceptionally strong when X is H_2SO_4, because almost without exception the colour produced by carbonyl compounds with (i) is more intense than with (ii) or (v) in the list of addenda given above. Unfortunately, there is no method of measuring the attachment of sulphuric acid to the carbonyl oxygen atom. However, according to the ionic theory, the greater the strength of an acid, the more easily is the acidic hydrogen ionised, and therefore the greater the amount of its free affinity. Consequently, carbonyl compounds should form more intensely coloured additive compounds with strong acids than with weak acids of similar constitution. This deduction, which can also be reached by a consideration of Werner's dissociation theory, has been proved by Stobbe and Haertel's experiments on salts of distyryl ketone, etc., and on the colours of solutions of a given ketone in acid having different dissociation constants (Abstr., 1910, i, 43).

When the negative constituent Y of an acid HY unites with a molecule B, forming HY···B, a little consideration shows that the carbonyl carbon atom is more unsaturated in the additive compound RR′CO···HY···B than in RR′CO···HY; this explains why the hydrochlorides of carbonyl compounds are less coloured than the mercurichlorides and stannichlorides, and also why the acid salts of carbonyl compounds [which the author regards as being constituted like the mercurichlorides; for example, $(CHPh{:}CH)_2CO\cdots HCl,HCl$] are more coloured than the normal salts.

The author's explanation of the catalytic action of acids or metallic salts (*loc. cit.*) would be greatly strengthened if the unsaturated character of the "binary" compound of the acid or metallic salt and the carbonyl compound could be directly proved by the formation of a "ternary" compound by the addition of a third molecule at the carbonyl carbon atom. Such addition would neutralise more or less the free affinity of the carbon atom, and such "ternary" compounds would be less coloured than the "binary" compounds; thus yellow *disalicylaldehyde tin tetrabromide*,

$$\left.\begin{array}{l}OH\cdot C_6H_4\cdot CHO\\OH\cdot C_6H_4\cdot CHO\end{array}\right\rangle SnBr_4,$$

is easily converted by exposure to the air into a colourless *dihydrate*, $2C_6H_4(OH)\cdot CHO,SnBr_4,2H_2O$, and the orange-red additive compound of distyryl ketone and tin tetrachloride unites with benzene to form an orange-yellow *substance*, $2(CHPh{:}CH)_2CO,SnCl_4,C_6H_6$.

Meyer states that the additive compounds of metallic salts and quinones correspond completely with the similar compounds of ordinary ketones (Abstr., 1909, i, 395; 1910, i, 179). The author

considers, therefore, that the colour phenomena of quinhydrones, of meriquinonoid compounds, and of the compounds of quinones and alkali phenoxides are explicable by his theory of halochromy. In these cases the unsaturated carbonyl carbon atoms are present in a ring, and their influence on selective absorption is materially strengthened by the presence of the ethenoid linkings.

Triphenylmethyl halides form with metallic salts intensely coloured additive compounds, which are generally regarded as $CPh_3X\cdots M$. The methane carbon atom, therefore, becomes unsaturated (triphenylmethyl may be regarded as an extreme case) and chromophoric, and this class of additive compounds falls into line with the author's theory; also, in the triphenylmethane dyes the colour may depend essentially on the presence of the central unsaturated carbon atom, the action of which is increased by auxochromic OH and NH_2 groups.

Finally, by reasoning based on his researches on the molecular compounds of the tin series, the author arrives at conclusions regarding Walden's inversion which do not differ much from those recently expressed by Werner and by Fischer.

The preceding statements are illustrated by reference to compounds in the literature and to the following new substances, which are obtained, as a rule, by the direct interaction of the two components in a non-hydroxylic solvent, usually benzene, occasionally ether or chloroform. (When not given, the formula is normal.) *Disalicylaldehyde tin tetrachloride*, deep yellow crystals, m. p. 152°; *disalicylaldehyde tin tetrabromide*, deep yellow crystals, m. p. 100°; *salicylaldehyde hydrobromide*, $OH\cdot C_6H_4\cdot CHO,HBr$, unstable, yellow prisms; *di-*o*-methoxybenzaldehyde tin tetrachloride*, yellow, crystalline powder, m. p. 180—181°; *di-*o*-methoxybenzaldehyde tin tetrabromide*, yellow, crystalline powder, m. p. 131°; *di-*m*-hydroxybenzaldehyde tin tetrachloride* and the *tin tetrabromide* are yellow, crystalline substances; *di-*m*-methoxybenzaldehyde tin tetrachloride*, yellowish-grey powder; *dipiperonal tin tetrachloride*, yellow, crystalline powder, blackening at 130—190°; *dipiperonal tin tetrabromide*, pale yellow, crystalline powder, m. p. 150°; *di-*p*-dimethylaminobenzaldehyde tin tetrachloride* and also the *tin tetrabromide*, canary-yellow substances; *di-*o*-nitrobenzaldehyde tin tetrachloride*, colourless, prismatic needles, m. p. 80—120°; *di-*m*-nitrobenzaldehyde tin tetrachloride*, colourless, crystalline; *di-*p*-nitrobenzaldehyde tin tetrachloride*, pale yellow, prismatic needles containing C_6H_6, half of which is easily lost, substance then has m. p. 101°; *di-*m*-hydroxyacetophenone tin tetrachloride*, yellow, crystalline, m. p. 99°; *di-*p*-hydroxyacetophenone tin tetrachloride*, colourless, crystalline, m. p. about 190°, reddening at about 150°; *diphorone tin tetrachloride*, colourless crystals, m. p. about 142° (decomp.); *bis-dimethylpyrone tin tetrachloride*, colourless crystals, m. p. 232—235° (decomp.); *dixanthone tin tetrachloride*, sandy-yellow powder, m. p. 245°; *dibenzophenone tin tetrachloride*, colourless crystals; *bis-phenyl styryl ketone tin tetrachloride*, deep yellow crystals; *bis-distyryl ketone tin tetrachloride*, orange powder, m. p. 188° (decomp.); *bis-cinnamylideneacetophenone tin tetrachloride*, Bordeaux-red crystals, m. p. about 160° (decomp.); *bis-dicinnamylideneacetone tin tetra-*

chloride, black precipitate, decomp. below 100°; *dibenzoylpiperidide tin tetrachloride*, colourless, crystalline, m. p. about 213°; *dicinnamoylpiperidide tin tetrachloride*, colourless leaflets, m. p. 221°; *dipiperine tin tetrachloride*, deep yellow crystals; *dipiperine tin tetrabromide*, deep yellow crystals, m. p. 183° (decomp.); *piperine stannichloride*, $2C_{17}H_{19}O_3N.H_2SnCl_6$, compact, yellow crystals (from alcohol containing hydrogen chloride); *piperine stannibromide*, $2C_{17}H_{19}O_3N,H_2SnBr_6$, compact, deep yellow crystals, m. p. 182—184° (decomp.); *piperine hydrochloride*, $C_{17}H_{19}O_3N,HCl$, canary-yellow, crystalline; *piperine dihydrochloride*, $C_{17}H_{19}O_3N,2HCl$, orange powder; *piperine hydrobromide*, $C_{17}H_{19}O_3N,HBr$, canary-yellow, crystalline, m. p. about 170°. Attempts to prepare a substance, $2CPh_3Cl,SnCl_4$, yield only Kehrmann's triphenylmethyl chloride tin tetrachloride, $CPh_3Cl,SnCl_4$.

C. S.

Modification of the Friedel and Crafts' Reaction Admitting of the Preparation of α-Naphthyl Ketones to the Exclusion of the β-Isomerides. E. CAILLE (*Compt. rend.*, 1911, **153**, 393—394).—A solution of the acid chloride in carbon disulphide is cooled to 0°, and treated with aluminium chloride in small portions at a time; crystals separate, consisting of a compound of the ketone with aluminium chloride; after about twenty-four hours these are collected, and decomposed with ice-water acidified with hydrochloric acid. The resulting ketone consists entirely of the α-naphthyl derivative, and the yield is 60—80%.

W. O. W.

2-Methyl-laurenone. A New Ketone Derived from Camphor. RENÉ LOCQUIN (*Compt. rend.*, 1911, **153**, 284—287. Compare Tiemann, Abstr., 1901, i, 5).—When the lactone, $C_{10}H_{16}O_4$, obtained by Baeyer and Villiger (Abstr., 1900, i, 133) in the oxidation of camphor with Caro's acid is heated with 20% phosphoric acid at 190—200°, it loses carbon dioxide and forms *2-methyl-laurenone* (2 : 3 : 3 : 4-*tetramethyl*-Δ^1-cyclo*pentenone*-5), $\begin{matrix}CMe_2\cdot CHMe \\ | \\ CMe=\!=\!=CH\end{matrix}\!\!>\!CO$, b. p. 82—86°/10 mm., 95—96°/18 mm., D_0^4 1·062. The constitution of this substance was established by its conversion by successive oxidation and esterification into *ethyl γ-keto-αββ-trimethylvalerate*, $COMe\cdot CMe_2\cdot CHMe\cdot CO_2Et$, b. p. 105—107°/12 mm., which forms a *semicarbazone*, m. p. 158—159°, and on treatment in the usual way yields the corresponding trimethylsuccinic acid.

2-Methyl-laurenone forms two *semicarbazones*, m. p. 150° and 198° respectively, a normal *oxime*, m. p. 95—96°, b. p. 122—128°/10 mm.; the *phenylcarbanilidoxime* has m. p. 101—102°. When treated with sodium and alcohol, it yields 1 : 2 : 2 : 3-*tetramethyl*-4-cyclo*pentanol*, $C_9H_{18}O$; the *phenylurethane* has m. p. 113—114°. 1 : 2 : 2 : 3-*Tetramethyl*-4-cyclo*pentanone*, b. p. 178—180°, forms two *semicarbazones*, m. p. 182° and 232° respectively.

W. O. W.

Some New Derivatives of *cyclo*Hexanones. ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1911, **46**, 662—669. Compare Abstr., 1901, i, 341; Thole and Thorpe, Trans., 1911, **99**, 422).—The *imide*

of *aa'-dicyanocyclohexane-1 : 1-diacetic acid*,

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH(CN)\cdot CO\\CH(CN)\cdot CO\end{matrix}>NH,$$

prepared from *cyclo*hexanone and ethyl cyanoacetate, crystallises in colourless needles, m. p. 211—212°. The *ammonium* salt is the primary product. When treated with bromine water, the imide yields quantitatively an additive product containing two atoms of bromine, m. p. 164—165° (with evolution of bromine). This *dibromide* when heated on a water-bath with 50% formic acid until effervescence ceases yields *aβ-dicyano-aβ-cyclohexanesuccinimide*,

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}C(CN)\cdot CO\\ | \\C(CN)\cdot CO\end{matrix}>NH,$$

which crystallises in lustrous needles, m. p. 238—240°. The removal of bromine from the dibromide can also be effected by warming it in aqueous-alcoholic solution.

1-Methyl*cyclo*hexan-3-one yields similar products.

The *imide* of *aa'-dicyano-1-methylcyclohexane-3 : 3-diacetic acid*, $CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2—CH_2\end{matrix}>C<\begin{matrix}CH(CN)\cdot CO\\CH(CN)\cdot CO\end{matrix}>NH$, has m. p. 240—241° (becoming brown; on Maquenne block the m. p. is 244—245°). The *ammonium* salt crystallises well. The imide absorbs two atoms of bromine, and the *dibromide* yields *aβ-dicyano-aβ-1-methylcyclohexane-3 : 3-succinimide*, $CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2—CH_2\end{matrix}>C<\begin{matrix}C(CN)\cdot CO\\ | \\C(CN)\cdot CO\end{matrix}>NH$, m. p. 241—242° (Maquenne block). R. V. S.

"Tagayasan," a Japanese Wood the Dust of which Causes Inflammation. K. Iwakawa (*Arch. expt. Path. Pharm.*, 1911, 65, 315—324).—Workmen dealing with Tagayasan timber suffer from inflammation of the eyes. The active principle was extracted by means of benzene, and appears to be identical with chrysophanohydroanthrone, $C_{15}H_{12}O_3$ (compare Abstr., 1900, i, 42), which, however, had not hitherto been found to occur naturally. The pure substance causes the same symptoms as the wood dust. E. J. R.

Synthesis of Linear Diphthaloylbenzene. Ernst Philippi (*Monatsh.*, 1911, 32, 631—635).—The anhydride of pyromellitic acid condenses with benzene in presence of aluminium chloride to a mixture of 4 : 6-dibenzoyl*iso*phthalic acid and 2 : 5-dibenzoylterephthalic acid. These are separated by making use of their solubility in water and nitrobenzene.

Both isomerides are converted on heating with concentrated sulphuric acid into linear diphthaloylbenzene,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2<\begin{matrix}CO\\CO\end{matrix}>C_6H_4.$$

4 : 6-*Dibenzoyl*iso*phthalic acid* crystallises in colourless needles or long plates, m. p. 263—264° (darkening).

2 : 5-*Dibenzoylterephthalic acid* crystallises in long, lanceolate plates or slender needles, which soften at 295°, m. p. 307—309°. On distillation with calcium oxide in a stream of hydrogen under reduced

pressure, *p*-dibenzoylbenzene is obtained; this confirms the constitution.

Diphthaloylbenzene crystallises in bunches of yellow needles, which are not altered at 370°, but sublime at a higher temperature. It forms a dark red vat with alkaline hyposulphite, and dyes cotton first green and then dark blue. E. F. A.

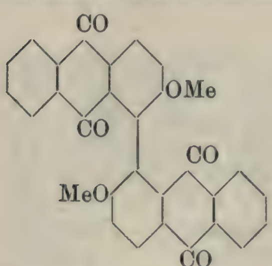
New Method of Formation of Flavanthren. ERWIN BENESCH (*Monatsh.*, 1911, 32, 447—456).—Flavanthren has been synthesised by the following series of reactions, starting from the methyl ether of 2-hydroxyanthraquinone, which is converted through the *nitro*- and *amino*-derivatives into 1-*iodo*-2-*methoxyanthraquinone*. This, when heated with copper powder, gives 2 : 2′-*dimethoxy*-1 : 1′-*dianthraquinonyl*, which after hydrolysis is converted by ammonia into 2 : 2′-diamino-1 : 1′-dianthraquinonyl; this last changes spontaneously into flavanthren.

On nitration of 2-methoxyanthraquinone, two isomeric mononitro-derivatives, m. p. 271° and 225°, are obtained. The less fusible isomeride does not form flavanthren, and is possibly 3-nitro-2-methoxyanthraquinone.

1-*Nitro*-2-*methoxyanthraquinone* forms yellow crystals, m. p. 271°.

3-*Nitro*-2-*methoxyanthraquinone*, m. p. 225°, is somewhat darker in colour and more soluble than the isomeride.

1-*Amino*-2-*methoxyanthraquinone* is red, and has m. p. 224°. The isomeric 3-*amino*-derivative has m. p. 218—222°.



1 - *Iodo* - 2 - *methoxyanthraquinone* forms lustrous, brown crystals, m. p. 265°. The 3-*iodo*-isomeride has m. p. 210—212°.

2 : 2′-*Dimethoxy*-1 : 1′-*dianthraquinonyl* (annexed formula) is a yellow powder, m. p. 346°. On hydrolysis by means of anhydrous aluminium chloride, 2 : 2′-*dihydroxy*-1 : 1′-*dianthraquinonyl* is obtained as a green, amorphous powder. The yields in these operations are but small, and flavanthren itself was not isolated, but its presence was definitely characterised. E. F. A.

Constitution of Camphene. II. Camphene Hydrochloride and Camphene Hydrate. OSSIAN ASCHAN (*Annalen*, 1911, 383, 1—38. Compare Abstr., 1910, i, 709).—Since there are at present two competing formulæ, namely, the author's "ethylene" formula and Wagner's "methylene" formula, for camphene, the question of the individual nature of the terpene acquires great importance. The author attempts, admittedly without much success, to answer it by converting camphene (from various sources) through the hydrochloride into camphene hydrate, regenerating camphene therefrom, and comparing the physical properties of the regenerated and the original camphenes. In the course of his experiments, which include the examination of pinene hydrochloride and bornyl and *iso*bornyl chlorides, the author obtains evidence which indicates that (1) crude

camphene hydrochloride is a mixture of two stereoisomerides, α and β, derived from camphene ("ethylene" formula), thus:

$$C_8H_{14}<\begin{matrix}CH\\ \| \\ CH\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CH_2\\ | \\ CHCl\end{matrix} \text{ and } C_8H_{14}<\begin{matrix}CHCl\\ | \\ CH_2\end{matrix};$$

(2) α-camphene hydrochloride, which is not decomposed by dilute aqueous potassium hydroxide, is the main constituent of bornyl chloride, whilst β-camphene hydrochloride is the chief constituent of *iso*bornyl chloride.

Thus camphene (prepared from the hydrochloride of rectified American turpentine), b. p. 159·5—160°, m. p. 40·5—41·5°, and $[\alpha]_D^{20}$ +12·85° in benzene, is converted by ethereal hydrogen chloride into crude camphene hydrochloride, m. p. 137—140°, and $[\alpha]_D$ −6·40°. This hydrochloride in benzene is shaken with dilute (approximately 3%) aqueous potassium hydroxide for twelve hours at 60°, and again for twelve hours at 80—90° after the addition of more potassium hydroxide, whereby is obtained camphene hydrate (from the α-camphene hydrochloride), b. p. 206—207·5°, m. p. 149°, $[\alpha]_D$ −2·89° in benzene, together with some camphene (from the β-camphene hydrochloride), b. p. 159·5—160·5°, m. p. 43—44°, D_{50}^{50} 0·8579, $[\alpha]_D^{20}$ +10·92° in benzene. When boiled with acetic anhydride and sodium acetate, the camphene hydrate yields, together with a little *iso*bornyl acetate, a camphene, b.p. 159—161°, m. p. 44—45°, $[\alpha]_D^{20}$ +12·63° in benzene, D_{50}^{50} 0·8531, and n_D^{50} 1·45952. Finally, the camphene hydrate in benzene is converted by hydrogen chloride into the original camphene hydrochloride, m. p. 151—153·5° (after recrystallisation from methyl alcohol containing hydrogen chloride), and $[\alpha]_D^{20}$ −6·495° in benzene. (Camphene hydrate would be expected to form only α-camphene hydrochloride; probably the hydrogen chloride acts as a dehydrating agent, producing camphene, which then unites with the acid to form the mixture of α- and β-camphene hydrochlorides.) The fact that the two camphenes, obtained in the preceding transformations agree very closely with the original camphene in physical properties indicates that the terpene is an individual substance.

Similar results have been obtained with a camphene (from Siberian pine-needle oil), b. p. 159—159·5°, m. p. 47—48°, D_{50}^{50} 0·8548, and $[\alpha]_D^{50}$ −89·29°. A liquid portion of the camphene, b. p. 159—160°, D_{15}^{15} 0·8728, and $[\alpha]_D$ −75·96°, is converted into the hydrochloride, m. p. 137° (crude) and 149—150° (recryst. from benzene), and $[\alpha]_D^{15}$ 47·33° in benzene, which yields by hydrolysis with dilute potassium hydroxide at 60°, and finally at 80°, camphene hydrate, $[\alpha]_D$ −1·35° in benzene, from which sodium acetate and boiling acetic acid regenerate a camphene, b. p. 161—163°, m. p. 49·5—51°, and $[\alpha]_D^{20}$ −76·04° in benzene.

When hydrolysed by dilute potassium hydroxide under the preceding conditions, bornyl chloride (from the *l*-borneol of Siberian pine-needle oil) yields camphene hydrate, m. p. 148—149°, and a trace of camphene, whilst *iso*bornyl chloride (from technical *iso*borneol) yields camphene, b. p. 159—160°, m. p. 50—51°, $[\alpha]_D^{20}$ −0·45° in benzene, and a trace of camphene hydrate. This evidence is the reason for statement (2) above.

Pinene hydrochloride (from American turpentine), m. p. 126°, $[\alpha]_D^{20}$ 6·65°, is scarcely attacked by 2% potassium hydroxide below 100°, but is hydrolysed by a mixture of alcohol, benzene, and milk of lime at 135° and finally at 150°, yielding 7—9% of camphene, b. p. 159·5—161°, m. p. 40—41°, $[\alpha]_D^{20}$ +14·52° in benzene, and less than 40% of camphene hydrate, b. p. 206—206·5°, m. p. 149—150°, $[\alpha]_D^{20}$ −3·24° in benzene; the camphene obtained from the hydrate by acetic anhydride and potassium acetate has b. p. 159·5—160°, m. p. 43—44°, D_{50}^{50} 0·8542, and $[\alpha]_D^{20}$ +15·43° in benzene. Similar results are obtained with a strongly active pinene hydrochloride (from Grecian turpentine), m. p. 128—130°, and $[\alpha]_D^{20}$ +28·88° in benzene; the camphene hydrate obtained therefrom has m. p. 149—150° and $[\alpha]_D^{20}$ −21·79° in benzene, and yields camphene, b. p. 159—160°, m. p. 44—45°, and $[\alpha]_D^{20}$ +85·68° in benzene. There is no doubt, therefore, that the camphene hydrate from pinene hydrochloride is identical with that from camphene hydrochloride.

The higher fractions of the products of the preceding hydrolyses contain chlorine, showing that crude camphene hydrochloride, bornyl chloride, and *iso*bornyl chloride contain a third constituent which is unattacked by 3% potassium hydroxide at 60—80°; it is also resistant to aniline at the ordinary temperature, but is hydrolysed by hot aniline and by alcoholic potassium hydroxide.

Attempts to separate the α- and the β-forms of camphene hydrochloride by crystallisation from petroleum have yielded the less soluble and more stable α-modification, which has m. p. 150—151° in its racemic form and 157—158° in its strongly active form (that from *l*-bornyl chloride). The presence of the β-modification in crude camphene hydrochloride and also in bornyl and *iso*bornyl chlorides is indicated by the rate of hydrolysis of these chlorides by alcoholic potassium hydroxide; the results are expressed graphically.

Camphene hydrate is converted almost quantitatively into *iso*bornyl acetate by heating with sulphuric and acetic acids and a little water at 60—70°. C. S.

Constitution of Camphene. III. Individuality of Camphene from Various Sources. OSSIAN ASCHAN (*Annalen*, 1911, 383, 39—51. Compare preceding abstract).—Samples of camphene from seven different sources have been oxidised by potassium permanganate essentially by the process described previously (Abstr., 1910, i, 709), and the products have been separated into their constituents (camphenilone, camphene glycol, camphenilic acid, sodium salt of an *acid*, m. p. 138°, camphenic acid, and other acids soluble in water) always under exactly the same conditions, so that the quantities of each constituent are comparable. It is found in all seven cases that the quantities of the chief oxidation products are, in general, nearly the same, and that the quantities of camphenilic acid and camphenic acid stand in a definite ratio to one another, 1 : 10. These results not only indicate that camphene is an individual substance, but also furnish strong evidence in favour of the author's "ethylene" formula. If camphene has Wagner's "methylene" formula, the formation of the chief oxidation product, camphenic acid, must be explained by

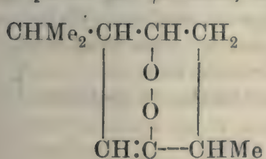
assuming an intramolecular change, whereby a five-membered ring becomes a six-membered ring. On the other hand, accepting the "ethylene" formula of camphene, the formation of camphenic acid is a direct process, and the production of the relatively small amount of camphenilic acid (and also of camphenilone and camphene glycol) is explicable by the more rational assumption of the change of a six-membered to a five-membered ring. C. S.

Constitution of Camphene. IV. Stereoisomeric Camphenic Acids. OSSIAN ASCHAN (*Annalen*, 1911, 383, 52—68. Compare preceding abstracts).—*cis-dl*-Camphenic acid is partly transformed into trans-dl-*camphenic acid*, $C_8H_{14}(CO_2H)_2$, m. p. 122—123° (*diamide*, m. p. 231—232°; dianilide, m. p. 165°), by distillation under 5 mm. pressure, or by heating for twelve hours at 180° with equal parts of acetic acid and 38% hydrochloric acid; the two modifications are separated by alcoholic sodium ethoxide, the sodium salt of the *trans*-acid being the more soluble. The two modifications in approximately equal amounts are also obtained by the reduction of *cis*-α-bromocamphenic acid by zinc and acetic and hydrochloric acids.

The conversion of *cis*-camphenic acid in a normal way into the *trans*-modification is important, since it furnishes a fairly certain proof that the migrating carboxyl group is attached to a ring carbon atom.

The distillation of *cis*-camphenic acid under ordinary pressure yields products which are receiving further examination. C. S.

Chemical Investigation of the Oil of Chenopodium. E. K NELSON (*J. Amer. Chem. Soc.*, 1911, 33, 1404—1412).—This oil is obtained by distillation of *Chenopodium ambrosioides* var. *Anthelmintica*. It contains about 70% of ascaridole (Abstr., 1908, i, 667), b. p. 96—97°/8 mm., D_{20}^{20} 0·9985, n_D^{20} 1·4769, a_D^{20} +0·7°. [The pure compound may be optically inactive, and this slight activity may be due to a trace of *d*-camphor (see below)]. Ascaridole readily undergoes rearrangement to form a glycol anhydride analogous to pinene oxide, a change indicating that it is an unstable dioxide. Further evidence is afforded by its property of exploding when heated, and by the violence of its reaction with ferrous sulphate and other reagents. The annexed constitution is assigned to it.



The author prepared *ascaridole glycol* (b. p. 271—272°, m. p. 62·5—64°, D_{20}^{20} 1·0981, n_D^{20} 1·4796, a_D 0) by treatment with ferrous sulphate, also the *monobenzoate*, m. p. 136—137°, and the *dibenzoate*, m. p. 116·5—117·5°, of the glycol.

An old sample of the oil was found to contain *d*-camphor.

E. J. R.

Dithiocamphorcarboxylic Acid. LÉO TSCHUGAEFF and G. PIGOULEWSKY (*Compt. rend.*, 1911, 153, 388—390).—This substance was obtained in an unsuccessful attempt to prepare a xanthate of the

camphor series. Sodium camphor, prepared by means of sodamide, was treated successively with carbon disulphide and methyl sulphate. After heating on the water-bath, the mixture gave *methyl dithiocamphorcarboxylate*, $C_8H_{14}<\begin{matrix}CH\cdot CS_2Me\\ | \\ CO\end{matrix}$, as a deep yellow oil, b. p. 179°/8 mm., D^{24} 1·1204, $[\alpha]_D$ +424·58°. The substance is remarkably stable, and has b. p. about 300° under ordinary pressure, practically without decomposition. Alcoholic potassium hydroxide converts it into potassium camphorcarboxylate. *Dithiocamphorcarboxylic acid* is a yellow oil, decomposing on heating into camphor and carbon disulphide. The *copper* salt is deep brown. W. O. W.

Decomposition of Terpenoid Substances by Glowing Metallic Wires. CARL D. HARRIES and KURT GOTTLOB (*Annalen*, 1911, **383**, 228—229).—An apparatus, termed the "isoprene lamp," is figured and described. A coil of platinum wire, 120 cm. in length and resistance 9Ω at an average red heat, is suspended in the neck of a flask and heated electrically (about 5 amperes at 220 volts). The flask is provided with a vertical condenser containing water at 50°. The liquid in the flask is gently boiled; the undecomposed vapour is condensed and returns to the flask, whilst the volatile decomposition products escape, and are condensed by a freezing mixture. Commercial *r*- or *l*-pinene yields only about 1% of isoprene, whilst commercial carvene yields 30—50%, according to the amount of limonene it contains. C. S.

Butadienes and Some Synthetic Caoutchouc Obtained Therefrom. CARL D. HARRIES (*Annalen*, 1911, **383**, 157—227).—The older processes for the synthesis of isoprene are condemned either on account of the rarity of the initial material, or because the resulting isoprene is contaminated with trimethylethylene or *as*-dimethylallene. The following process is adopted to obtain pure isoprene in quantity sufficient for the determination of its physical constants.

[With KARL NERESHEIMER.]—Ethyl pyrotartrate is reduced by sodium and alcohol to *iso*pentane-$\alpha\delta$-diol,

$$OH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot OH,$$

b. p. 124—125°/13 mm., D_{18}^{18} 0·9954, n_D^{18} 1·45173 (*diacetate*, b. p. 116—117°/17 mm., D_{20}^{20} 1·0434, n_D^{20} 1·42717; *oxide*, $\begin{matrix}CHMe\cdot CH_2\\ | \\ CH_2—CH_2\end{matrix}>O$, b. p. 86—87°, D_{20}^{20} 0·8643, n_D^{20} 1·41122; s-*diphenyldiurethane*, m. p. 97°; *tetraphenyldiurethane*, m. p. 102°). The glycol is converted by 60% hydrobromic acid at 100° into $\alpha\delta$-dibromo-β-methylbutane (Abstr., 1907, i, 743), b. p. 84—86°/11 mm., D_{17}^{17} 1·6986, n_D^{17} 1·51217, which reacts with 33% alcoholic trimethylamine at 100° to form the corresponding bis-quaternary ammonium bromide, the base of which, by distillation, yields isoprene (in 50% yield), b. p. 36—37°, D_{21}^{21} 0·6804, D_4^{21} 0 6793, n_D^{21} 1·42267, n_α^{21} 1·41807, n_γ^{21} 1·44340.

For the technical preparation of isoprene, Hofmann's (Elberfeld)

process with *p*-cresol is recommended as giving very pure isoprene. The author obtains most of his (pure) isoprene by heating turpentine or, better, dipentene or limonene over a glowing platinum spiral (preceding abstract), but also obtains a fair amount by dropping $\beta\gamma$-dibromo-β-methylbutane (obtained from acetone through the amyl alcohol) on soda-lime at 600°. The soda-lime is advantageously previously saturated with carbon dioxide (the reagent thus prepared is more porous than calcium carbonate or similar substances), and the process, for which a special apparatus has been designed, is applicable to the preparation of other homologous hydrocarbons. When heated with quinoline, $\beta\gamma$-dibromo-β-methylbutane is converted into a substance, b. p. 39—40°, D_4^{17} 0·6719, n_D^{17} 1·40188, which probably consists chiefly of *as*-dimethylallene.

Erythrene ($\Delta^{\alpha\gamma}$-butadiene) is conveniently obtained from phenol by the Elberfeld process. A satisfactory laboratory method starts from *sec.*-butyl alcohol. This is converted by phosphoric oxide into the olefine, the dibromide of which yields butadiene by the hot soda-lime process.

$\beta\gamma$-Dimethyl-$\Delta^{\alpha\gamma}$-butadiene can be obtained by the author's method with pinacone hydrochloride and hot soda-lime, but is best prepared from pinacone and potassium hydrogen sulphate by the Elberfeld process.

Each of the preceding butadienes yields by suitable polymerisation a "normal" caoutchouc and a "sodium" caoutchouc, which are similar in appearance, but differ in their behaviour with ozone.

"Normal" caoutchoucs are obtained when the polymerisation is effected by the acetic acid process or, better, by heat alone, as in the Elberfeld method. Experiments with "normal" isoprene caoutchouc show that in order to secure a product of good quality it is necessary, not only to use pure isoprene, but also to exclude oxygen during the process of polymerisation. Synthetic caoutchoucs are very sensitive to autoxidation, and the higher the temperature of polymerisation, the more readily does the caoutchouc undergo autoxidation.

The quality of a synthetic caoutchouc is conveniently tested by submitting the caoutchouc to a process of cold vulcanisation (the hot process requires costly apparatus and a large amount of material, and is unsuitable for laboratory experiments), and examining the solidity and elasticity of the product. As tested by this method, the best synthetic caoutchouc is produced when isoprene is polymerised by heat alone at the lowest possible temperature.

The comparison of synthetic with natural caoutchouc is very difficult, because only the nitrosites and tetrabromides are available for comparative purposes, and these compounds are amorphous, difficult to purify, and have no definite m. p. The author, therefore, prefers to rely on a comparison of the ozonides and of their products of decomposition. He thus finds that "normal" isoprene caoutchouc (and, still more distinctly, "normal" dimethylbutadiene caoutchouc) must contain a small amount of another caoutchouc, because the decomposition products of its ozonide contain some substances (methylglyoxal ?) which are not found among the products of decomposition of the ozonide

of natural caoutchouc. Moreover, a small portion of the synthetic caoutchouc is very much more difficultly ozonised than is natural caoutchouc. The constitution $\left[CMe{<}{\begin{matrix}CH{\cdot}CH_2{\cdot}CH_2\\CH{:}CH{-}CH_2\end{matrix}}{>}CHMe\right]_x$ or $\left[CMe{<}{\begin{matrix}CH{\cdot}CH_2{-}CH_2\\CH{:}CH{\cdot}CHMe\end{matrix}}{>}CH_2\right]_x$ is suggested for the second synthetic caoutchouc.

A comparison of "normal" isoprene caoutchouc and purified Para caoutchouc with regard to their behaviour with Budde's brominating solution shows that hydrogen bromide is more copiously evolved during the reaction of the synthetic caoutchouc, and that the resulting tetrabromide is easily and completely soluble in carbon disulphide.

The action of nitrous fumes on "normal" isoprene caoutchouc yields, as in the case of natural caoutchouc, a yellowish-green, insoluble *nitrosite* "*a*," decomp. 115—120° or 130—135°, and a soluble *nitrosite* "*c*," decomp. 158—162°, the composition of which approximates to the formula $C_{10}H_{15}O_7N_3$ less exactly than does that of the nitrosite "*c*" of carefully purified natural caoutchouc, which also has decomp. 158—162°. When distilled in a vacuum, the synthetic caoutchouc behaves like natural rubber, and so also when treated with ozone (with the two reservations mentioned above).

When heated in glacial acetic acid at 110—120° for ten days, $\Delta^{\alpha\gamma}$-butadiene yields "normal" *butadiene-caoutchouc*, $(C_8H_{12})_x$, a pure product being obtained when oxygen is excluded during the polymerisation. This caoutchouc resembles gelatin, is non-elastic and easily torn, and is sparingly soluble except in chloroform. It forms a yellow, amorphous, easily soluble *nitrosite*, decomp. above 80°, and yields an explosive, oily *ozonide* (in chloroform), or a white, solid ozonide (in carbon tetrachloride), the latter closely resembling the ozonide of $\Delta^{1:5}$-*cyclo*octadiene. When polymerised by heat alone, butadiene yields a solid, the distillation of which at 100—110°/0 mm. furnishes a *hydrocarbon*, C_8H_{12}, b. p. 36°/23 mm., D_4^{16} 0·8523, n_D^{16} 1·46768, which resembles the terpenes. The residue contains the caoutchouc, which is quite similar to that obtained by the acetic acid process, except that it is insoluble even in chloroform, and is unaffected by nitrous acid or ozone.

Dimethylbutadiene polymerises very much more slowly than isoprene. The acetic acid process yields a yellow, friable product. When heated in a sealed tube at 100° for about twenty-three days, dimethylbutadiene is converted into a viscous mass, which is distilled at ordinary pressure to remove the unchanged hydrocarbon, and then at 110°/0 mm. to separate the small amount of terpene by-product. An ethereal solution of the residue yields, by the addition of alcohol, "normal" *dimethylbutadiene-caoutchouc*, $(C_{12}H_{20})_x$, which can scarcely be distinguished from isoprene caoutchouc in its external appearance. It can be vulcanised, and forms a *tetrabromide*, $C_{12}H_{20}Br_4$, evolving hydrogen bromide at about 130°, and a *nitrosite*, $C_{12}H_{19}O_7N_3$, darkening at 120°. When ozonised in carbon tetrachloride, it gives a mixture of two *ozonides*, the decomposition of which by hot glacial acetic acid yields acetonylacetone and other substances which reduce Fehling's solution.

"Sodium" *butadiene-caoutchouc*, $(C_8H_{12})_x$, is obtained almost quantitatively when $\Delta^{\alpha\gamma}$-butadiene is heated with a little sodium wire in a sealed

tube at 35—40° for three hours, and the resulting viscous, brown mass is washed with dilute alcohol. When freshly prepared, it is pale yellow, transparent, and soluble in ether, chloroform, and benzene, but it loses these properties after keeping, and becomes viscous and stringy. It can be vulcanised (hot or cold process), yielding a product which surpasses all other synthetic caoutchoucs in elasticity. The *nitrosite* (approximately $C_8H_{12}O_3N_2$) and *bromide* (approximately $C_8H_{12}Br_4$) are described. In chloroform, 6—7% ozone produces an impure, oily *diozonide*, $C_8H_{12}O_6$, whilst 12—14% ozone produces a very explosive *substance*, which is apparently an ozonide, $C_8H_{12}O_4$; the decomposition products of these substances are being examined.

"Sodium" *isoprene-caoutchouc*, $(C_{10}H_{16})_x$, is obtained almost quantitatively by heating pure isoprene with sodium at 60° for about fifty hours. It resembles the "normal" caoutchouc in its physical properties (except appearance), but is more soluble. It can be vulcanised, forms a white *tetrabromide* very similar to the "normal" tetrabromide, and yields with nitrous acid a mixture of two *nitrosites*, one insoluble, the other soluble; the latter is a yellowish-white powder, darkening at 170—180°. The "sodium" caoutchouc in carbon tetrachloride is attacked very slowly by 12—14% ozone, and yields a mixture of an ozonide and diozonide. With 6—7% ozone in chloroform, it forms a solid *diozonide*, $C_{10}H_{16}O_6$, which is quite different from the diozonide of ordinary caoutchouc, since its products of decomposition do not give the pyrrole reaction, and do not contain any characteristic substance except a very small amount of lævulaldehyde.

"Sodium" *dimethylbutadiene-caoutchouc*, obtained by heating dimethylbutadiene with sodium at 60° for ten to twelve days and nights, forms, after purification, a mass like gutta-percha. Its behaviour with ozone is similar to that of "sodium" isoprene caoutchouc; evidence of the presence of the "normal" caoutchouc is also obtained. The *tetrabromide* is a white powder, which evolves hydrogen bromide at 130°; the *nitrosite* is also described.

The paper concludes with some remarks on the constitution of natural caoutchouc and a reply to Pickles' criticisms (Trans., 1910, **97**, 1085). C. S.

Chemistry of Caoutchouc. II. Physico-chemical Investigation of the Extraction of Resin. David Spence and J. H. Scott (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 83—85. Compare this vol., i, 657).—Measurements have been made of the quantities of resin extracted from caoutchouc by boiling acetone during successive equal intervals of time. When the percentage of extracted resin is plotted against time, a curve is obtained which closely resembles the corresponding curve representing Bayliss's data for the rate of extraction of salts from gelatin by water. From this, it appears probable that a portion, at least, of the resin is present in the caoutchouc in the adsorbed condition.

Reference is made to the extraction experiments of Zilchert (*Gummi Zeit.*, 1911, **25**, 716), in which different kinds of caoutchouc were examined. The differences met with are supposed by the authors to

be due to differences in the degree of dispersity of the colloidal system. H. M. D.

New Synthetic Glucosides. EMIL FISCHER and BURCKHARDT HELFERICH (*Annalen*, 1911, **383**, 68—91. Compare Abstr., 1910, i, 716).—With the object of obtaining as many synthetic glucosides as possible for comparison with natural products, the authors have applied König and Knorr's process to geraniol, *cyclo*hexanol, benzyl alcohol, cetyl alcohol, and ethyl glycollate. In every case except the last two the glucosides are split by emulsin, and therefore belong to the β-series; there is no doubt that the two exceptions also belong to the same series. The same method is used for each alcohol, except in the case of ethyl glycollate, where a solvent is not employed. The alcohol and bromoacetoglucose dissolved in ether are shaken for several hours with freshly prepared dry silver oxide until a filtered sample no longer gives a precipitate of silver bromide when boiled with aqueous silver nitrate.

*Tetra-acetyl-β-benzyl-*d*-glucoside*, $CH_2Ph\cdot C_6H_7O_6Ac_4$, white needles, m. p. 96—101° (corr.), has $[\alpha]_D^{22}$ $-49{\cdot}51°$ in alcohol, and is hydrolysed by aqueous barium hydroxide to *β-benzyl-*d*-glucoside*,

$$CH_2Ph\cdot O\cdot C_6H_{11}O_5,$$

flexible needles, m. p. 123—125° (corr.), $[\alpha]_D^{20}$ $-55{\cdot}76°$ in water, which has a very bitter taste, does not reduce Fehling's solution, and is rapidly hydrolysed by dilute hydrochloric acid or emulsin.

*Tetra-acetyl-β-*cyclo*hexyl-*d*-glucoside*, $C_6H_{11}\cdot C_6H_7O_6Ac_4$, long needles, m. p. 120—121° (corr.), $[\alpha]_D^{22}$ $-29{\cdot}74°$ in alcohol, yields *β-*cyclo*hexyl-*d*-glucoside*, $C_6H_{11}\cdot O\cdot C_6H_{11}O_5$, m. p. 133—137° (corr.), $[\alpha]_D^{20}$ $-41{\cdot}55°$ in water, by hydrolysis as above. *Tetra-acetyl-β-geranyl-*d*-glucoside*, $C_{10}H_{17}\cdot C_6H_7O_6Ac_4$, white needles, m. p. 29—30°, $[\alpha]_D^{22}$ $-25{\cdot}17°$ in alcohol, is hydrolysed by aqueous alcoholic barium hydroxide, yielding *β-geranyl-*d*-glucoside*, $C_{10}H_{17}\cdot O\cdot C_6H_{11}O_5,H_2O$, long needles, m. p. 58°, $[\alpha]_D^{27}$ $-38{\cdot}12°$ in water. *Tetra-acetyl-β-cetyl-*d*-glucoside*,

$$C_{16}H_{33}\cdot O\cdot C_6H_7O_5Ac_4,$$

glistening needles, m. p. 71—73° (corr.), $[\alpha]_D^{20}$ $-20{\cdot}19°$ in alcohol, is not attacked by dilute hydrochloric or sulphuric acid, and is hydrolysed by boiling alcohol and 10% sodium hydroxide, yielding *β-cetyl-*d*-glucoside*, $C_{16}H_{33}\cdot O\cdot C_6H_{11}O_5$, colourless needles, $[\alpha]_D^{24}$ $-22{\cdot}02°$ in alcohol, which is tasteless, melts indefinitely between 110° and 145°, is not attacked by Fehling's solution, by dilute mineral acids, or by emulsin, but is hydrolysed on the water-bath by acetic acid containing a few drops of hydrochloric acid. *Ethyl tetra-acetyl-β-*d*-glucosidoglycollate*, $CO_2Et\cdot CH_2\cdot O\cdot C_6H_7O_5Ac_4$, colourless needles, m. p. 83—84° (corr.), $[\alpha]_D^{20}$ $-40{\cdot}62°$ in alcohol, is hydrolysed by $N/5$-barium hydroxide in twenty hours, yielding *β-*d*-glucosidoglycollic acid*, $CO_2H\cdot CH_2\cdot O\cdot C_6H_{11}O_5$, clusters of stout leaflets, m. p. 165—167°, $[\alpha]_D^{21}$ $-44{\cdot}11°$ in water, which has an acid taste, is not attacked by Fehling's solution or emulsin, and forms amorphous *calcium*, *barium*, *zinc*, *lead*, and *mercury* salts, and a crystalline *sodium* salt. *β-*d*-Glucosidoglycollamide*, $NH_2\cdot CO\cdot CH_2\cdot O\cdot C_6H_{11}O_5$, obtained by saturating with ammonia a methyl-alcoholic solution of ethyl tetra-acetylglucosidoglycollate in a freezing mixture, has m. p. 167° (corr.)

and $[\alpha]_D^{18} -43\cdot24°$, is hydrolysed by boiling dilute hydrochloric acid or by emulsin, and has a sweet taste and bitter after-taste; attempts to prepare the corresponding nitrile by boiling acetic anhydride result in the formation of *penta-acetylglucosidoglycollamide*, $C_{18}H_{25}O_{12}N$, white needles, m. p. 146—149° (corr.).

Pentabenzoyldextrose ($[\alpha]_D^{20} +25\cdot40°$ in chloroform) reacts like penta-acetyldextrose with hydrogen bromide in glacial acetic acid, forming *bromo-β-benzoglucose*, $C_6H_7O_5Bz_4Br$, white needles, m. p. 125—128° (corr.), $[\alpha]_D^{19} +145\cdot1°$ in toluene, which interacts with methyl alcohol and silver oxide to produce *tetrabenzoyl-β-methyl-*d-*glucoside*, $CH_3\cdot C_6H_7O_6Bz_4$, white needles, m. p. 160—162° (corr.), $[\alpha]_D^{20} +30\cdot99°$ in chloroform; the last substance is converted into β-methylglucoside by shaking with alcoholic sodium ethoxide. C. S.

The Glucoside of Leaves of the Pear Tree, its Presence in the Leaves of Different Varieties, its Detection in the Trunk and Root. ÉMILE BOURQUELOT and (Mlle.) A. FICHTENHOLZ (*Compt. rend.*, 1911, 153, 468—471. Compare Abstr., 1910, i, 273; ii, 742).—Arbutin has been obtained from the leaves of four new varieties of pear tree in addition to those already studied. Probably all varieties of *Pirus* contain arbutin. This glucoside also occurs in the trunks and roots of the trees. W. O. W.

Bile Pigments. I. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1911, 73, 204—239).—Maly's hydrobilirubin and the urobilin described by Garrod and Hopkins (Abstr., 1896, i, 712) are shown to be mixtures. Hæmopyrrole is not the urobilinogen of the urine; the urobilin prepared from hæmopyrrole has quite different properties from that of urine.

Bilirubin dissolves to form colloidal solutions in presence of taurocholic and glycocholic acids. When reduced by means of sodium amalgam, bilirubin forms *hemibilirubin*, $C_{16}H_{22}O_3N_2$ or $C_{16}H_{20}O_3N_2$, crystallising in short, colourless prisms, which tend to become red and belong to the monoclinic system [$a:b:c = 1\cdot8:1:0\cdot7$; $\beta = 110°20'$], m. p. 192° (decomp.). It gives an intense red coloration with sodium hydroxide and copper sulphate, forms dyes with diazonium salts, and changes on exposure to the air, first to a reddish-orange dye and then to a brown dye with a green surface reflex: these show all the urobilin reactions.

A new biliary acid, *lithocholic acid*, $C_{24}H_{40}O_3$, is isolated from ox gall stones. This crystallises in long prisms, m. p. 184—186° (corr.), $[\alpha]_D^{20} +32\cdot14°$; it is tasteless, and crystallises from acetic acid without a molecule of the solvent.

The composition of coprosterol given by Bondzynski and Humnicki is confirmed; this has m. p. 112—116°, $[\alpha]_D^{20} +24\cdot53°$.

Deoxycholic acid was obtained from fæces in colourless needles, m. p. 145°, $[\alpha]_D^{20} +53\cdot38°$. E. F. A.

Hypericin (Hypericum Red). C. ČERNÝ (*Zeitsch. physiol. Chem.*, 1911, 73, 371—382. Compare Wolff, *Pharm. Centr.-h.*, 1875, 16, 193).—The flowers of *Hypericum perforatum* contain a brilliant red

pigment in addition to a yellow pigment. The red colouring matter has an absorption spectrum very similar to that of oxyhæmoglobin. About 1 gram of pigment has now been isolated from 2470 grams of dried flowers having approximately the formula $C_{16}H_{10}O_5$; the possibility of it being a flavone dye is suggested. Solutions of hypericin in organic solvents are blood-red; on dilution they become somewhat violet, and show a fire-red fluorescence. Measurements have been made of the absorption spectrum under various conditions in extension of those of Wolff (*loc. cit.*). E. F. A.

Constitution of Divalolactone. SIMA M. LOSANITSCH (*Compt. rend.*, 1911, **153**, 390—392).—Fittig (Abstr., 1890, 286) regarded divalolactone, the product of the action of sodium ethoxide on valerolactone, as an ether containing two lactonic oxygen atoms. The present author believes the third atom of oxygen to be ketonic, and the substance to have the formula $\begin{array}{l}CO\text{———}CH\cdot CO\cdot C_4H_7\\ |\qquad\qquad\quad |\\ O\cdot CHMe\cdot CH_2\end{array}$. Fittig's divalolactonic acid would then have the constitution

$$OH\cdot CHMe\cdot CH_2\cdot CH(CO_2H)\cdot CO\cdot C_4H_7.$$

The following observations support these conclusions: Magnesium methyl iodide acts on valerolactone, giving *βε-dihydroxy-β-methylhexane*, b. p. 121°/14 mm., whereas divalolactone does not give the analogous diol, but loses water, forming *dimethylanhydrovalolactone*, $C_{12}H_{20}O_2$, b. p. 104—105°/13·5 mm. This is a ketone, since on further treatment with magnesium methyl iodide, it yields a *compound*, $C_{13}H_{24}O_2$, b. p. 136—137°/13 mm., whilst the analogous ether, 2 : 5 : 5-*trimethyltetrahydrofuran*, b. p. 102—103°, does not react with the Grignard reagent. On treating divalolactonic acid with methyl sulphate and sodium hydroxide, it yields, according to conditions, the corresponding *methyl* ester, b. p. 114°/13 mm., or divalolactone.

The C_4H_7 group in these compounds is under investigation.

W. O. W.

Catalytic Preparation of Substituted Ketohydrofurans. GEORGES DUPONT (*Compt. rend.*, 1911, **153**, 275—277. Compare this vol., i, 554).—The conversion of dimethyl-Δ^{γ}-hexinene-βε-diol into a tetrahydrofuran derivative by the catalytic action of mercuric sulphate has been extended to other diols of the type

$$OH\cdot CRR'\cdot C\vdots C\cdot CRR'\cdot OH.$$

When R and R′ are saturated and of low molecular weight, the change is rapid and quantitative, but secondary reactions intervene when the radicles are unsaturated, aromatic, or of high molecular weight.

The following *diols* are new: *Acetylenediacraldehyde*,

$$CH_2\!:\!CH\!:\!CH(OH)\cdot C\vdots C\cdot CH(OH)\cdot CH\!:\!CH_2,$$

b. p. 146°/15 mm., D^{24} 1·0341, n_D 1·5040; *acetylenedicrotonaldehyde*, $CHMe\!:\!CH\cdot CH(OH)\cdot C\vdots C\cdot CH(OH)\cdot CH\!:\!CHMe$, m. p. 90—92°; the *tetrabromide* has m. p. 137°; *acetylenediisovaleraldehyde*,

$$CH_2Pr^{\beta}\cdot CH(OH)\cdot C\vdots C\cdot CH(OH)\cdot CH_2Pr^{\beta},$$

b. p. 158—160°/15 mm., D^{24} 0·92475, n_D 1·4614; *acetylenedibutyrone*, $OH\cdot CPr_2\cdot C\vdots C\cdot CPr_2\cdot OH$, pearly spangles, m. p. 120°.

3-*Keto*-2 : 5-*dimethyltetrahydrofuran* has b. p. 143°, D^{15} 0·9894, n_D 1·4267 ; the *compound*, $C_6H_6(SO_4Hg_2O)$, was isolated as an intermediate product in its formation. Pinacone gives a similar *compound*, $C_6H_{10}(SO_4Hg_2O)$, when treated with Denigès' reagent. The new ketone reduces Fehling's solution, and gives a *semicarbazone*, m. p. 168—170°. 3-*Keto*-2 : 5-*dimethyl*-2 : 5-*diethyltetrahydrofuran*, b. p. 192°, D^{15} 0·9317, n_D 1·4368, forms a *semicarbazone*, m. p. 136—138°. 3-*Keto*-2 : 5-*diisobutyltetrahydrofuran*, b. p. 112—114°/15 mm., D^{24} 0·9066, n_D 1·4385. 3-*Keto*-2 : 2 : 5 : 5-*tetraethyltetrahydrofuran*, b. p. 110°/18 mm., D^{24} 0·9275, n_D 1·4486. 3-*Keto*-2 : 5-*dipentamethylenetetrahydrofuran*, $C_3H_6<\substack{CH_2\\CH_2}>C<\substack{CO\cdot CH_2\\—O—}>C<\substack{CH_2\\CH_2}>C_3H_6$, has b. p. 152—154°/18 mm., D^{24} 1·0268, n_D 1·4904 ; the *semicarbazone* has m. p. 216°. W. O. W.

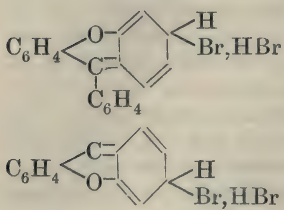
Condensation of *p*-Dibromobenzene with Xanthone ; Quinocarbonium Salts. LEE H. CONE and C. J. WEST (*J. Amer. Chem. Soc.*, 1911, 33, 1538—1548).—By the action of xanthone on the products resulting from dibromobenzene and magnesium, p-*phenylenedixanthenol*, $\left(O<\substack{C_6H_4\\C_6H_4}>C\cdot OH\right)_2C_6H_4$, is formed in addition to *p*-bromophenylxanthenol (Gomberg and Cone, Abstr., 1909, i, 55; 1910, i, 869). This is the simplest member of a new series of xanthenols with two reactive nuclei ; with hydrochloric acid a coloured diacid chloride and a colourless normal dichloride are formed. The influence of the bridge oxygen is brought to light by a comparison with tetraphenyl-*p*-xylylene glycol, $OH\cdot CPh_2\cdot C_6H_4\cdot CPh_2\cdot OH$ (Thiele and Balhorn, Abstr., 1904, i, 491).

This glycol gives with hydrogen bromide in acetic acid solution a colourless bromide, which with metallic silver or copper yields a quinonoid orange-coloured hydrocarbon, tetraphenyl-*p*-xylylene, which is not at all an analogue of triphenylmethyl.

p-Phenylenedixanthenol gives with hydrogen chloride a coloured dihydrochloride, from which a colourless simple chloride can be prepared. Silver removes the chlorine from this chloride, forming an unsaturated hydrocarbon, which is a true isologue of triphenylmethyl. A colourless bromide could not be obtained.

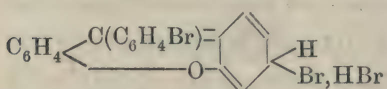
p-*Phenylenedixanthenol* forms colourless crystals, m. p. 176—177°. The *chloride-hydrochloride* is a bright red, crystalline powder ; on heating a suspension in benzene, hydrogen chloride is evolved and a clear, colourless solution of the *chloride*, $C_6H_4\left(CCl<\substack{C_6H_4\\C_6H_4}>O\right)_2$, remains. This darkens at 210°, m. p. 259—260°. It forms a number of salts characterised by their great insolubility and high melting points. The *ferrichloride* forms orange-red crystals ; the *zincichloride* is somewhat darker in colour ; the *stannichloride* separates in finely divided orange crystals ; the *mercurichloride* gives dull red crystals ; the *perbromide* forms yellow crystals ; the *periodide* is a dark brown, nearly black, powder ; the *perchlorate* separates in fine reddish-yellow crystals, and the *hydrogen sulphate* is a crystalline powder.

p-*Phenylenediquinoxanthenol bromide hydrobromide* (annexed formula) is obtained in reddish-brown crystals; the *bromide* is a red solid, and has not been obtained in a colourless form.



The following salts of *p*-bromophenylxanthenol are described: *ferrichloride*, orange-yellow needles, m. p. 218°; *zincichloride* double salt, large, shimmering, dark orange plates, m. p. 235°; *stannichloride*, dark yellow crystals, m. p. 185°; *mercurichloride*, light orange-yellow crystals, which turn bright yellow at 160°, soften at 250°, m. p. 257° to a dark liquid. The *perbromide* of the *chloride* forms fine glistening, light orange needles, m. p. 201—202°; the *periodide* appears in dark purple, shining needles, m. p. 188°. The *hydrogen sulphate* crystallises in large plates, which are brown in transmitted light, and have a green metallic lustre in reflected light, m. p. 77—78°.

p-*Bromophenylquinoxanthenol bromide hydrobromide* (annexed formula), prepared by the addition of acetyl bromide to a solution of the xanthenol, forms very hygroscopic, dark orange-red crystals. It loses hydrogen bromide, forming p-*bromophenylxanthenol bromide*, $C_{19}H_{12}OBr_2$, which is colourless.



The *zincibromide* separates in bright red crystals, m. p. 250° to a dark red liquid; the *mercuribromide* yields yellow crystals, m. p. 247—248° to a dark red liquid. The *bromide perbromide* is obtained as orange crystals, m. p. 188°; the *bromide periodide* forms deep purple, lustrous crystals, m. p. 211—212° to a dark purple liquid.

E. F. A.

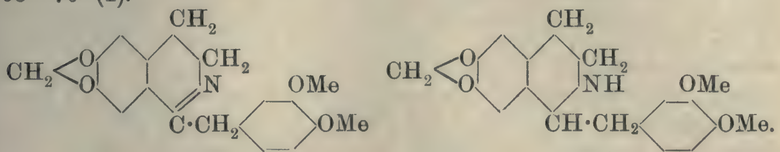
5-Methylthiophen-2-aldehyde. E. Grishkewitsch-Trochimowsky (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 803—806. Compare this vol., i, 481).—In ethereal solution, 2-iodo-5-methylthiophen readily reacts with magnesium, forming the corresponding iodomagnesium derivative, which, when treated with ethyl orthoformate, yields the *acetal*, $\begin{matrix} CMe\text{—}S \\ \| \\ CH\cdot CH \end{matrix}\!\!>\!C\cdot CH(OEt)_2$, as a colourless, viscous liquid with a pleasant fruity odour, b. p. 236·5—238°/747 mm., $D_4^{19\cdot5}$ 1·0388, $n_D^{19\cdot5}$ 1·48953.

5-*Methylthiophen-2-aldehyde*, $\begin{matrix} CH{=\!=}CMe \\ | \\ CH{:}C(CHO) \end{matrix}\!\!>\!S$, obtained by hydrolysing the acetal with hydrochloric acid in a current of carbon dioxide, is a colourless, refractive liquid with an odour of bitter almonds, b. p. 218—219·5°/749 mm., D_4^{21} 1·1698, n_D^{21} 1·58166. Its *phenylhydrazone*, $C_{12}H_{12}N_2S$, forms faintly yellow needles, m. p. 116—117°.

An ethereal solution of the aldehyde saturated with ammonia in the cold gradually deposits the *hydramide*, $(C_4H_2SMe\cdot CH{:})_3N_2$, in rosettes of colourless needles, m. p. 124·5—125·5°; the hydramide is decomposed into its components when gently heated with dilute mineral acid.

The action of carbon dioxide on the above iodo-magnesium complex gives 5-methylthiophen-2-carboxylic acid in almost quantitative yield. T. H. P.

Synthesis of Berberine. AMÉ PICTET and ALPHONSE GAMS (*Compt. rend.*, 1911, **153**, 386—388; *Ber.*, 1911, **44**, 2480—2485. Compare this vol., i, 483).—The complete synthesis of berberine has now been accomplished in the following steps. Homopiperonylamine condenses with homoveratroyl chloride to give *homoveratroylhomopiperonylamine*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}C_6H_3(OMe)_2$, long needles, m. p. 136°. This loses $1H_2O$ when boiled with phosphoric oxide in xylene solution, and forms the unsaturated *compound*, m. p. 68—70° (I).



(I.) (II.)

Reduction of this tertiary base with tin and hydrochloric acid leads to the formation of *veratrylnorhydrohydrastinine*, slender needles, m. p. 208—210° (II). A methylene group is introduced between the imino-group and the veratryl ring by condensing the product with methylal in presence of hydrochloric acid. The tetrahydroberberine so obtained is identical with that prepared by Perkin from natural berberine, and yields this substance when treated with oxidising agents. W. O. W.

The Alkaloids of the Toadstool and "Artificial" Muscarine. J. HONDA (*Arch. expt. Path. Pharm.*, 1911, **65**, 454—466).—A method is described by which muscarine can be obtained from toadstools and freed from the choline also invariably present. In addition to these two substances, two other alkaloids were also isolated, and named *α*- and *β-myketosine*. The quantities obtained were too small for analysis.

The muscarine thus isolated has the same physiological action as "artificial" muscarine obtained by the oxidation of choline platinichloride. E. J. R.

Cyclic Ammonium Bases. HERMAN DECKER and ADOLF KAUFMANN (*J. pr. Chem.*, 1911, [ii], **84**, 219—246).—The first part of this paper is mainly a review of previous work on the constitution of the ψ-ammonium bases. This is followed by a discussion of the subjects enumerated below.

(I) *Constitution of the Carbinol Bases.*—The author criticises the view that the ψ-ammonium bases have an aldehydic or ketonic structure. The formation of anhydrides of the carbinol bases observed by Kaufmann and Strübin (this vol., i, 321) furnishes no evidence in support of the aldehydic structure. Reference is made to the formation of symmetrical ethers of carbinol bases of other classes,

and the preparation of the *anhydride* of 2-hydroxy-9-phenylxanthen-9-ol, $(C_{19}H_{13}O_2)O$, m. p. 246°, is described.

(II) *Constitution of the Cyanines.*—In this section the author discusses the constitution of the cyanine dyes, and explains the mechanism of the reactions by which they are formed.

(III) *The Negative Properties of the Nitrogen Atom in Aromatic Rings.*—The substitution processes occurring in heterocyclic rings are readily explicable on the assumption that the nitrogen atom exercises an orientating influence, similar to that of a strongly negative group, such as the nitro-group. The mobility of the atoms or groups in the 2- or 4-position of the pyridine ring is referred by the author to the same negative property of the nitrogen atom.

(IV) *Constitution of the* apo*Cyanines.*—The negative influence referred to in the preceding section is the factor which determines the formation of the *apo*cyanines. Owing to this negative property of the nitrogen atom, the hydrogen occupying the 2-position in the quinoline molecule is very reactive, and condensation, therefore, readily takes place in this position. Kaufmann and Strübin's (this vol., i, 328) assumption that 1 : 2-dihydroquinoline is an intermediate product in the formation of the *apo*cyanine dyes thus becomes unnecessary.

(V) *The Aldehydic Function of Carbinol Bases.*—In this section attention is drawn to the great similarity in the reactions of aldehydes and carbinol bases, and to the remarkable activity of the hydroxyl group.

(VI) *The Cause of the Aldehydic Function of Carbinol Bases.*—A comparison of the formulæ of the aldehyde-ammonias (I) and the ψ-ammonium bases (II) at once reveals the fact that these compounds are similarly constituted :

$$\underset{\text{(I.)}}{R{\cdot}CH{<}^{NH_2}_{OH},} \qquad \underset{\text{(II.)}}{R{\cdot}CH{<}^{NR'R''}_{OH}.}$$

It is to this similarity of structure that the remarkable resemblance in the reactions of aldehydes and ψ-ammonium bases is due. F. B.

The Splitting of the Pyrrolidine Ring by Bacteria. DANKWART ACKERMANN (*Zeitsch. Biol.*, 1911, 57, 104—111).—*dl*-Proline, obtained by the hydrolysis of gelatin with baryta according to Fischer and Boehner's method, was acted on by a mixed culture of putrefaction bacteria in a culture solution containing Witte's peptone and dextrose. The solution was kept slightly alkaline. If the decomposition proceeded in the manner usual for amino-acids, pyrrolidine should be formed, but this substance could not be detected ; instead, the ring was broken and δ-aminovaleric acid was formed by the addition of two atoms of hydrogen. Arginine is also decomposed by bacteria with formation of the same acid. E. J. R.

The Reactivity of the β-Unsubstituted Pyrrole Ring. W. KÖNIG (*J. pr. Chem.*, 1911, [ii], 84, 194—219).—The reactions of β-unsubstituted indole and pyrrole derivatives are compared with those of primary amines and of compounds containing a reactive

methylene group. It is shown that there is a remarkable resemblance in the chemical behaviour of these three groups.

Guided by this similarity, the author attempted to prepare 2-methylindole-3-aldoxime by heating a methyl-alcoholic solution of 2-methylindole with mercury fulminate and hydrochloric acid, but obtained, instead of the aldoxime, the mercurichloride of a red dye, which proved to be identical with that prepared by Ellinger and Flamand (this vol., i, 329) from 2-methylindole-3-aldehyde and dilute sulphuric acid. From the analysis of numerous salts, and from quantitative experiments on the formation of the perchlorate and mercurichloride, as well as from many other considerations, the author conclusively proves that the dye base has the composition $C_{19}H_{16}N_2$, and not $C_{28}H_{23}N_3$, as stated by Ellinger and Flamand. When heated with phenylhydrazine, it yields 2-methylindole and 2-*methylindole*-3-*aldehydephenylhydrazone*, $NH<\substack{C_6H_4 \\ CMe}>C\cdot CH:N\cdot NHPh$, which crystallises in lustrous, colourless needles, m. p. 201°. Both this reaction and the similar decomposition by hydrolysis into 2-methylindole and 2-methylindole-3-aldehyde are in agreement with the formula, $NH<\substack{C_6H_4 \\ CMe}>C\cdot CH:C<\substack{C_6H_4 \\ CMe}>N$, proposed by the author.

The dyes are therefore derivatives of 3 indyl-3-indolidenemethane, and not of tri-indylmethane, as supposed by Ellinger and Flamand.

The *mercurichloride*, $C_{19}H_{17}N_2Cl,HgCl_2$, crystallises with one molecule of methyl alcohol in large, apparently rhombic plates with a green lustre, m. p. 197°; these lose their methyl alcohol at 120°, and are transformed into red needles having a violet lustre. The *mercuribromide*, prepared from 2-methylindole, mercury fulminate, and hydrobromic acid, forms brownish-red crystals, also containing one molecule of methyl alcohol, m. p. 193°.

Similar mercurihalides have been obtained from 2:5-dimethylindole and 2-phenyl-5-methylpyrrole.

2-*Methylindole-3-aldoxime*, $C_{10}H_{10}ON_2$, prepared by heating the aldehyde with hydroxylamine hydrochloride and pyridine, crystallises in long, colourless needles, m. p. 154°. When boiled with acids, it is slowly converted into the above-mentioned dye; the transformation takes place much more readily in the presence of mercuric chloride.

The salts of the dye are best prepared by the addition of a slight excess of the requisite acid to 2-methylindole-3-aldehyde dissolved in six to eight times its weight of alcohol. The *hydrochloride*,

$$C_{19}H_{16}N_2,HCl,$$

m. p. 248°; the *hydrobromide*, m. p. 218°; the *hydriodide*, m. p. 228—230°, and the *perchlorate*, $C_{19}H_{16}N_2,HClO_4$, m. p. 248° (decomp.), all crystallise in red or brownish-red needles containing one molecule of methyl alcohol; the sulphate, m. p. 215° with previous sintering, has the composition $C_{19}H_{16}N_2,H_2SO_4$ (compare Ellinger and Flamand, *loc. cit.*).

A general method for the preparation of the dyes of the 3-indyl-3-indolidenemethane series is described. Ethyl orthoformate (1 mol.) and indole or its derivatives (2 mols.) are dissolved in the smallest possible quantity of alcohol and treated with the calculated amount

of the acid, the salt of which is required. The following compounds were prepared in this manner: the *perchlorate* of the dye from indole (3-indyl-3-indolidenemethane),

$$NH<\substack{C_6H_4\\ -CH}>C\cdot CH:C<\substack{C_6H_4\\ -CH}>N,HClO_4,$$

crystallising in ruby-red needles with a green lustre, m. p. 276°; the corresponding sulphate (compare Ellinger and Flamand, Abstr., 1909, i, 846), and the *perchlorate*, $C_{21}H_{20}N_2,HClO_4$, from 2:5-dimethylindole; the latter compound crystallises with one molecule of alcohol in long, bright red needles, which lose their alcohol at 120°, and have m. p. 245°.

Similar salts have been prepared from 1-alkylindoles, 2-phenyl-5-methylpyrrole, and 3-methylindole.

The dyes of this series are also obtained in small yield by the action of hydrocyanic acid and hydrogen chloride on indole and its derivatives in the presence of aluminium chloride. F. B.

p-**Hydroxybenzylamine.** MARC TIFFENEAU (*Bull. Soc. chim.*, 1911, [iv], **9**, 819—824. Compare this vol., i, 778).—The author has undertaken the investigation of this phenolic base and of certain of its homologues in view of their close connexion with hordenine, and analogous substances, of marked physiological activity (compare Barger, Trans., 1909, **95**, 1123, 2193, and Barger and Walpole, *ibid.*, p. 1720).

p-Hydroxybenzylamine, prepared from anisylamine by the action of hydriodic acid, was used in the form of the *hydrochloride*, m. p. 195°; the *hydriödide* melts at 198—200°.

2-p-*Methoxybenzyl*-1 : 3-*dihydro*iso*indole*,

$$C_6H_4<\substack{CH_2\\ CH_2}>N\cdot CH_2\cdot C_6H_4\cdot OMe,$$

m. p. 83°, obtained by von Braun's method (Abstr., 1910, i, 506) from *o*-xylylene bromide and anisylamine, crystallises in needles, and is very soluble in alcohol; the *hydrobromide*, m. p. 234°, crystallises in spangles, and the *methiodide* has m. p. 183°. When boiled with acetic anhydride, anisyl acetate and 2-*acetyl*-1 : 3-*dihydro*iso*indole*, $C_6H_4<\substack{CH_2\\ CH_2}>NAc$, m. p. 77°, b. p. 180—200°/15 mm., are formed. The latter crystallises in needles from boiling light petroleum. T. A. H.

Hydrazones. ROBERTO CIUSA and L. VECCHIOTTI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 803—807. Compare Abstr., 1910, i, 196).—The *p*-nitrophenylhydrazones of benzaldehyde, and *o*-, *m*-, and *p*-nitrobenzaldehyde exhibit chromoisomerism similar to that previously discussed. The *p*-nitrophenylhydrazone of anisaldehyde, however, was not obtained in two modifications. Benzaldehyde-*p*-nitrophenylhydrazone (compare Hyde, Abstr., 1899, i, 688) when recrystallised from alcohol forms orange needles, m. p. 195—196°. When precipitated from warm alcohol with water, it is transformed into yellow scales, m. p. 195°. If, however, the precipitation is effected in the cold, a red form is obtained in needles or scales, which become yellow at 140° and melt at 194°. The yellow variety can be transformed into

the other by recrystallisation from formamide, from which solvent only the red form is deposited. The red and yellow modifications thus appear to be distinct, whilst the orange-coloured products, which can be prepared by the action of various solvents, represent one or more mixtures, combinations, or solid solutions of these two.

o-Nitrobenzaldehyde-*p*-nitrophenylhydrazone when recrystallised from glacial acetic acid forms orange-red needles, which become red at 190°, and melt at 250—251°. By precipitation with water from alcohol, it is converted into an orange-yellow modification, m. p. 250—251°.

m-Nitrobenzaldehyde-*p*-nitrophenylhydrazone (Hyde, *loc. cit.*) crystallises from acetic acid in orange-red crystals, m. p. 250—251°, which, by precipitation with water from alcohol, are converted into the yellow form, m. p. 248°. This form when heated to 130° acquires an increasing red tint, but regains its original colour on cooling (thermochromism).

p-Nitrobenzaldehyde-*p*-nitrophenylhydrazone (Hyde, *loc. cit.*) crystallises from glacial acetic acid in brick-red scales, m. p. 247°. From alcohol an orange-yellow form, m. p. 245°, is obtained.

Anisaldehyde-p-*nitrophenylhydrazone* forms small, reddish-violet needles, m. p. 160°; only one modification could be isolated, but the addition of water to its solution in acetone gives a yellow precipitate which becomes red immediately. R. V. S.

Isomeric Hydrazones of Dithiocarbonic Esters. MAX BUSCH and HERMANN KRAPF (*J. pr. Chem.*, 1911, [ii], 84, 293—304).—It has been shown previously (Abstr., 1901, i, 430) that the phenylhydrazones of unsymmetrical esters of dithiocarbonic acid exist in two stereoisomeric forms, $\begin{array}{c}\mathrm{RS{\cdot}C{\cdot}SR'}\\ \Vert\\ \mathrm{N{\cdot}NHPh}\end{array}$ and $\begin{array}{r}\mathrm{RS{\cdot}C{\cdot}SR'}\\ \Vert\\ \mathrm{NHPh{\cdot}N}\end{array}$, which appear to be equally stable. In extending the investigation to the *p*-tolylhydrazones and *p*-bromophenylhydrazones, the authors have met with a marked difference in the stability of the isomerides. Thus, of the isomeric *p*-tolylhydrazones of methyl *p*-nitrobenzyl dithiocarbonate, the more fusible modification is the less stable form, and is completely transformed at 100° into the less fusible, stable isomeride.

The isomeric hydrazones described below were prepared by successively introducing two different groups into *p*-tolyldithio carbazinic acid or *p*-bromophenyldithiocarbazinic acid by the action of alkyl or aryl halides on the potassium salts of the acids, or of their esters in aqueous alcoholic solution, at the ordinary temperature, the different modifications being produced by varying the order of introduction of the groups R′ and R″:

$$\mathrm{NHR{\cdot}NH{\cdot}CS_2H \longrightarrow NHR{\cdot}NH{\cdot}CS_2R' \longrightarrow NHR{\cdot}N{:}C(SR'){\cdot}SR''}.$$

The isomerides are distinguished by naming the two groups in the order in which they are introduced. It is assumed that the group first introduced and the hydrazine residue occupy the *anti*-positions.

The *phenylhydrazone* of *benzyl* o-*nitrobenzyl dithiocarbonate*, $\mathrm{C_7H_7{\cdot}S{\cdot}C(S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2){:}N{\cdot}NHPh}$, prepared from *o*-nitrobenzyl chloride and benzyl phenyldithiocarbazinate, crystallises in clusters of red needles, m. p. 67°. The isomeric o-*nitrobenzyl benzyl dithiothio-*

carbonate phenylhydrazone, prepared from benzyl chloride and *o*-nitrobenzyl phenyldithiocarbazinate, forms lustrous, light red columns, m. p. 88°. Both forms have the same solubility, and, when heated separately at 100°, are converted into a mixture consisting of the two isomerides in equal proportions.

The interaction of *p*-nitrobenzyl chloride and potassium *p*-tolyldithiocarbazinate yields p-*nitrobenzyl* p-*tolyldithiocarbazinate*,

$$C_7H_7\cdot NH\cdot NH\cdot CS_2\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

which crystallises in stout, yellow needles, m. p. 127°, together with the p-*tolylhydrazone* of *di*-p-*nitrobenzyl dithiocarbonate*,

$$C_7H_7\cdot NH\cdot N\colon C(S\cdot CH_2\cdot C_6H_4\cdot NO_2)_2\ ;$$

the latter compound forms lustrous, red, pointed needles, m. p. 116°

o-*Nitrobenzyl* p-*tolyldithiocarbonate*, prepared in a similar manner to the preceding *p*-nitro-compound, crystallises in yellow needles, m. p. 147°, which become green when kept. It is accompanied by *di*-o-*nitrobenzyl dithiocarbonate* p-*tolylhydrazone*, crystallising in very slender, felted, golden-yellow needles, m. p. 134°.

Methyl p-*nitrobenzyl dithiocarbonate* p-*tolylhydrazone*,

$$SMe\cdot C(S\cdot CH_2\cdot C_6H_4\cdot NO_2)\colon N\cdot NH\cdot C_7H_7,$$

prepared from methyl *p*-tolyldithiocarbazinate and *p*-nitrobenzyl chloride, forms lustrous, garnet-red, pointed needles, m. p. 115° ; the isomeric p-*nitrobenzyl methyl dithiocarbonate* p-*tolylhydrazone*, prepared by methylating *p*-nitrobenzyl *p*-tolyldithiocarbazinate, crystallises in tufts of glassy, golden-yellow needles, m. p. 57°. The former isomeride is the stable form, and remains unchanged when heated above its m. p.

Ethyl p-*nitrobenzyl dithiocarbonate* p-*tolylhydrazone*, $C_{17}H_{19}O_2N_3S_2$, crystallises in lustrous, red leaflets, m. p. 70° ; the *isomeride* is a red oil.

The p-*tolylhydrazone* of *benzyl* p-*nitrobenzyl dithiocarbonate*,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot C(S\cdot C_7H_7)\colon N\cdot NH\cdot C_7H_7,$$

prepared from *p*-nitrobenzyl chloride and benzyl *p*-tolyldithiocarbazinate, is identical with the hydrazone obtained by the interaction of benzyl chloride and *p*-nitrobenzyl *p*-tolyldithiocarbazinate ; it crystallises in tufts of red needles or garnet-red, quadrilateral plates, m. p. 119°.

o-*Nitrobenzyl* p-*nitrobenzyl dithiocarbonate* p-*tolylhydrazone*,

$$C_7H_7\cdot NH\cdot N\colon C(S\cdot CH_2\cdot C_6H_4\cdot NO_2)_2,$$

forms slender, orange needles, m. p. 124° ; the *isomeride*, light red columns, m. p. 80°.

p-*Nitrobenzyl* p-*bromophenyldithiocarbazinate*,

$$C_6H_4Br\cdot NH\cdot NH\cdot CS_2\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

crystallises in long, transparent, light yellow needles, m. p. 135—136° ; it is obtained together with the p-*bromophenylhydrazone* of *di*-p-*nitrobenzyl dithiocarbonate*, $C_6H_4Br\cdot NH\cdot N\colon C(S\cdot CH_2\cdot C_6H_4\cdot NO_2)_2$, which forms lustrous, red needles, m. p. 132°, by the interaction of *p*-nitrobenzyl chloride and potassium *p*-bromophenyldithiocarbazinate.

o-*Nitrobenzyl* p-*bromophenyldithiocarbazinate*, prepared in a similar manner, crystallises in slender, white needles, m. p. 156—157° ; the accompanying *di*-o-*nitrobenzyl dithiocarbonate* p-*bromophenylhydrazone* forms slender, felted, light red needles, m. p. 119°.

The p-*bromophenylhydrazone* of *methyl* p-*nitrobenzyl dithiocarbonate*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot S \cdot C(SMe):N \cdot NH \cdot C_6H_4Br$, could only be obtained in one form; it crystallises in slender, monoclinic prisms, capped with clinodomes or pyramids, and has m. p. 119° or 120—121°, according to the method of preparation.

o-*Nitrobenzyl* p-*nitrobenzyl dithiocarbonate* p-*bromophenylhydrazone*, $C_{21}H_{17}O_4N_4BrS_2$, crystallises in clusters of small, stout, golden-yellow needles, m. p. 113—114°; the *isomeride* forms felted, orange-red needles, m. p. 107°. When fused for some time, each modification yields a mixture of the two isomerides in approximately equal proportions.

The *benzoylphenylhydrazone* of *methyl ethyl dithiocarbonate*,

$$SMe \cdot C(SEt):N \cdot NPhBz,$$

prepared from methyl benzoylphenyldithiocarbazinate and ethyl iodide, crystallises from alcohol in colourless, transparent columns, m. p. 93°, and from light petroleum in pointed needles, m. p. 94°. The isomeric *ethyl methyl dithiocarbonate benzoylphenylhydrazone*, obtained from ethyl benzoylphenyldithiocarbazinate and methyl iodide, separates from alcohol in stout, white needles, m. p. 83—84°, and from light petroleum in hard needles of a diamond lustre, m. p. 85—86°.

F. B.

Hydantoins. IV. Reduction of Aldehyde Condensation Products of 2-Thio-1-phenylhydantoin. TREAT B. JOHNSON and CHARLES A. BRAUTLECHT (*J. Amer. Chem. Soc.*, 1911, 33, 1531—1538). —Wheeler and Hoffmann (this vol., i, 498) have shown that on condensation of hydantoin with aldehydes, unsaturated compounds are formed, which when warmed with hydriodic acid are reduced at the double bond and transformed quantitatively into alkyl-hydantoins. These are hydrolysed by acids or alkalis to the corresponding α-amino-acids.

2-Thio-1-phenylhydantoin likewise condenses with aldehydes, but its derivatives are not reduced at the double bond by hydriodic acid. Zinc dust and acetic acid, or ammoniacal ferrous sulphate, were also ineffective, but sodium amalgam effected a quantitative transformation into the alkylthiohydantoins. These compounds could not be hydrolysed by sodium or barium hydroxides to α-amino-acids.

2-Thio-1-phenyl-4-benzylidenehydantoin is attacked by chlorine and bromine in glacial acetic acid solution. 2-*Thio*-1-*phenyl*-4-α-*chlorobenzylidenehydantoin*, $NPh\left<\begin{matrix}CO \cdot C:CClPh \\ CS-NH\end{matrix}\right.$, crystallises in colourless prisms, m. p. 236—237°. The corresponding α-*bromobenzylidene* compound separates in yellow plates, m. p. 211°.

On reduction of 2-thio-1-phenyl-4-benzylidenehydantoin with sodium amalgam, the same 2-thio-1-phenyl-4-benzylhydantoin is obtained as is obtained by the interaction of phenylthiocarbamide and phenylalanine (Brautlecht).

On alkylation of this with ethyl bromide in presence of sodium ethoxide, 2-*ethylthiol*-1-*phenyl*-4-*benzylhydantoin* is formed as an oil, which when digested with hydrochloric acid is converted into 1-phenyl-4-benzylhydantoin.

2-*Thio*-1-*phenylhydantoin*-4-*glyoxylic acid*, $\begin{matrix}NPh\cdot CO\\ | \\ CS\text{--}NH\end{matrix}\!\!>\!CH\cdot CO\cdot CO_2H$, prepared by the interaction of ethyl oxalate and 2-thio-1-phenylhydantoin, crystallises in pale yellow needles, m. p. 240° (decomp.).

2-*Thio*-1-*phenyl*-4-p-*methoxybenzylhydantoin* crystallises in slender, colourless prisms, m. p. 171°.

2-*Thio*-1-*phenyl*-4-*piperonylhydantoin*,

$$\begin{matrix}NPh\cdot CO\\ | \\ CS\text{--}NH\end{matrix}\!\!>\!CH\cdot CH_2\cdot C_6H_3{:}O_2{:}CH_2,$$

is obtained in straw-coloured needles, m. p. 172—173°. E. F. A.

Compound of Antipyrine with Ferric Chloride, obtained with Ferrous Chloride. CHARLES ASTRE and J. VIDAL (*Bull. Soc. chim.*, 1911, [iv], 9, 836—839. Compare this vol., i, 399).—A solution of ferrous chloride to which antipyrine dissolved in hydrochloric acid has been added develops a gooseberry-red coloration, and on evaporation and treatment of the syrupy residue with ether, deposits yellowish-green crystals of a *substance* having the formula

$$(C_{11}H_{12}ON_2)_9,FeCl_3,9HCl.$$

This becomes pasty at 121—122°, and dissolves in water, forming a gooseberry-red solution, which becomes yellowish-green on addition of an acid, or enough alkali to neutralise it. The solution gives the usual reactions of ferric iron, antipyrine, and chlorides. The ferric iron is reduced to the ferrous state by sodium nitrite, hydrogen sulphide, or sulphur dioxide, but not by zinc and acetic acid. The compound is quite distinct from that with ferric chloride, called ferripyrine, described by Schuyten (Abstr., 1896, i, 575).

T. A. H.

Formation of 1-Nitroso-5-methyl-3-pyrazolidone from Crotonoylhydrazide. ERNST MUCKERMANN (*J. pr. Chem.*, 1911, [ii], 84, 278—292. Compare this vol., i, 682).—*Crotonoylhydrazide*, $CHMe{:}CH\cdot CO\cdot NH\cdot NH_2$, is obtained as a viscid liquid by the interaction of ethyl crotonate and hydrazine hydrate in alcoholic solution. It possesses the usual reducing properties, and forms a *hydrochloride*, crystallising in snow-white needles, m. p. 173° (decomp.). When treated with benzaldehyde it yields a *benzylidene* derivative,

$$CHMe{:}CH\cdot CO\cdot NH\cdot N{:}CHPh,$$

m. p. 72°; the o-*hydroxybenzylidene* derivative, $C_{11}H_{12}O_2N_2$, has m. p. 190°; the p-*methoxybenzylidene* derivative, $C_{12}H_{14}O_2N_2$, crystallises in yellowish-white needles, m. p. 99°.

Crotonoylsemicarbazide, $CHMe{:}CH\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2$, prepared by the interaction of crotonoylhydrazide hydrochloride and potassium cyanate in aqueous solution, crystallises in stout prisms, m. p. 171°.

When treated with sodium nitrite, the hydrazide hydrochloride is converted into 1-*nitroso*-5-*methyl*-3-*pyrazolidone*. This crystallises in lustrous, white leaflets, m. p. 131°, and gives a cherry-red coloration with ferric chloride; the *ammonium* salt, $C_4H_{10}O_2N_4,1\frac{1}{2}H_2O$, forms radiating needles, m. p. 144° (decomp.); the *silver* salt, $C_4H_6O_2N_3Ag$, long, lustrous, silky needles, m. p. 148—149° (decomp.); the *copper* salt, $Cu(C_4H_6O_2N_3)_2,2H_2O$, stout, dark blue, monoclinic prisms

[$a:b:c=1{\cdot}23:1:0{\cdot}85$; $\beta=101°30'$] (Beder). The ammonium salt forms with picric acid a *compound*, $C_4H_{10}O_2N_4,C_6H_3O_7N_3$, which crystallises with one molecule of ethyl alcohol in lustrous, golden-yellow, monoclinic columns, m. p. 162—164°.

1-*Nitroso-5-methyl-2-ethyl-3-pyrazolidone*, $C_6H_{11}O_2N_3$, obtained by the action of ethyl iodide on the above-mentioned silver salt, separates from ether in colourless, monoclinic plates, m. p. 83°.

When 1-nitroso-5-methyl-3-pyrazolidone is treated with bromine in glacial acetic acid solution below 10°, it yields 4-*bromo*-3-*methyl*-5-*pyrazolone*, $C_4H_5ON_2Br$, which crystallises in colourless, hexagonal platelets, m. p. 182°, and may also be obtained by brominating 3-methylpyrazolone (Curtius and Jay, Abstr., 1889, 393). The interaction of 1-nitroso-5-methyl-3-pyrazolidone and excess of bromine in glacial acetic acid solution yields 4 : 4-*dibromo-3-methyl-5-pyrazolone*, $C_4H_4ON_2Br_2$. This crystallises in short, monoclinic columns, m. p. 132°, and may also be prepared by brominating 3-methylpyrazolone (compare Rothenburg, Abstr., 1895, i, 686). The compound described by Rothenburg as 4 : 4-dibromo-3-methylpyrazolone of m. p. 182° is probably identical with the above-mentioned 4-bromo-3-methylpyrazolone. F. B.

Hydroxyindazoles. V. Constitution. PAUL FREUNDLER (*Bull. Soc. chim.*, 1911, [iv], 9, 778—784. Compare this vol., i, 577, 753).—Further proof is given of the constitution of the chlorinated hydroxyindazoles obtained from substituted benzeneazo-*o*-benzoic acids. The presence of an indazole nucleus is shown by the fact that 5 : 7-dichloro-3-hydroxy-2-phenylindazole yields, on treatment with phosphorus pentachloride in the presence of phosphoryl chloride, 3 : 5 : 7-*trichloro-2-phenylindazole*, needles, m. p. 172·5°. This substance can also be obtained by direct chlorination of 2-phenylindazole of known constitution.

The position of the hydroxyl group is shown in that on oxidation of the hydroxyindazole by moderate oxidising agents it is transformed into 2-*benzeneazo*-3 : 5-*dichlorobenzoic acid*, $N_2Ph{\cdot}C_6H_2Cl_2{\cdot}CO_2H$, red prisms, m. p. 142·5—143°, which is also obtained by the oxidation of the above-mentioned trichloro-compound. On reduction, it yields aniline and 3 : 5-dichloroanthranilic acid, thus proving the position of the chlorine atoms.

Further, the hydroxyindazole yields a *benzoyl* derivative, long needles, m. p. 203·5—204°, and a *methyl ether*, tabular prisms, m. p. 144—144·5°. W. G.

Crystallographical Examination of Inactive Ornithine Monopicrate. P. REINER (*Zeitsch. physiol. Chem.*, 1911, 73, 192—193).—The triclinic crystals of *dl*-ornithine monopicrate, m. p. 170° (compare Kossel and Weiss, Abstr., 1910, ii, 909), have $a:b:c=0{\cdot}6962:1:0{\cdot}6301$; $\alpha=93°10'$, $\beta=100°55'$, $\gamma=81°19'$. E. F. A.

Extractives of Muscles. XII. Constitution of Carnosine. WLADIMIR VON GULEWITSCH (*Zeitsch. physiol. Chem.*, 1911, 73, 434—446. Compare Skwarzoff, Abstr., 1910, ii, 879).—The author

has suggested (Abstr., 1907, i, 337) that the products of hydrolysis of carnosine by barium hydroxide are histidine and a substance $C_3H_7O_2N$, probably alanine.

It is now established that three-quarters of the carnosine-nitrogen belong to histidine and the rest to a substance which is not *dl*-α-alanine, but is proved to be β-alanine, m. p. 230—232°. Carnosine is accordingly β-alanylhistidine or histidyl-β-alanine, and may have been derived from asparagylhistidine or histidyl-lysine by the loss of an amino-group and elimination of a carbon atom, so that the β-alanyl residue is formed. E. F. A.

_N_-Amino-heterocyclic Compounds. III. Properties of α-Acylhydrazines, 1-Amino-2:5-diphenyl-1:3:4-triazole, and 1-Amino-2:5-dibenzyl-1:3:4-triazole. HARTWIG FRANZEN and F. KRAFT (*J. pr. Chem.*, 1911, [ii], 84, 122—139. Compare Franzen and Scheuermann, Abstr., 1908, i, 293).—The reactions previously described (*loc. cit.*) as characteristic of *as.-sec.*-hydrazines are also given by α-acylhydrazines, with the exception of the reaction with pyruvic acid. When α-acetyl- or α-benzoyl-phenylhydrazine is boiled with alcohol and precipitated mercuric oxide, the latter rapidly turns black, and dark-coloured oily products are obtained when the alcoholic solutions are evaporated. It has not been settled whether tetrazones are formed as intermediate products. α-Acetylphenylhydrazine forms a quaternary nitrogen derivative, namely, the *ethiodide*,

$$NH_2\cdot NEtPhAcI,$$

when heated with ethyl iodide at 100° for several hours; this crystallises from alcohol, and has m. p. 201°. α-Benzoylphenylhydrazine under similar conditions gives tarry products.

1-Amino-2:5-diphenyl-1:3:4-triazole (Pinner, Abstr., 1894, i, 386) and 1-amino-2:5-dibenzyl-1:3:4-triazole (Pinner, Abstr., 1897, i, 640) have been examined as further examples of *N*-amino-heterocyclic compounds. Their behaviour resembles that of similar compounds already studied (Abstr., 1906, i, 706; 1908, *loc. cit.*). They are not affected when boiled with alcohol and mercuric oxide, and do not condense with acetophenone, acetone, or pyruvic acid. The diphenyl derivative reacts slowly with aldehydes, for example, with benzaldehyde, it yields the benzylidene derivative, $C_2Ph_2N_3\cdot N\colon CHPh$, which forms salts with most acids.

Tertiary hydrazines can be obtained by reducing the condensation products of aromatic aldehydes and alcohol with *as.-sec.*-hydrazines by means of sodium amalgam; phenylbenzylbenzylidenehydrazine yields α-phenyl-$\alpha\beta$-dibenzylhydrazine, and dibenzylbenzylidenehydrazine yields tribenzylhydrazine. The condensation products of 1-amino-2:5-diphenyltriazole with aldehydes can be reduced in a similar manner.

The best yields of 1-amino-2:5-diphenyl-1:3:4-triazole are obtained by the action of an alcoholic solution of hydrogen chloride on diphenyldihydrotetrazine. Its *picrate*, $C_{20}H_{15}O_7N_7$, separates from alcohol in brilliant yellow crystals, m. p. 154°.

The *hydrochloride* of the benzylidene derivative,

$$\left.\begin{matrix}N\!\!=\!\!=\!\!=\!\!CPh \\ | \\ N(HCl)\colon CPh\end{matrix}\right>N\cdot N\colon CHPh,$$

has m. p. 175°; it cannot be recrystallised, as it readily loses hydrogen chloride. The *sulphate*, $2C_{12}H_{16}N_4,H_2SO_4$, has m. p. 178°; the *nitrate*, m. p. 166°; the *picrate*, $C_{27}H_{19}O_7N_7$, crystallises from alcohol in slender, yellow needles, m. p. 169°; the *platinichloride* forms an orange-coloured precipitate, m. p. 231°.

αβ-Dibenzyl-α-phenylhydrazine hydrochloride,

$$CH_2Ph\cdot NPh\cdot NH\cdot CH_2Ph,HCl,$$

crystallises from alcohol, and has m. p. 186°; the corresponding *base*, $C_{20}H_{20}N_2$, solidifies slowly, crystallises from ether, has m. p. 42°, and decomposes on exposure to the air, giving an odour of benzaldehyde. When boiled with alcohol and mercuric oxide, it is oxidised to phenylbenzylbenzylidenehydrazone, and the same product appears to be formed by the action of dilute nitric acid or of picric acid on the base.

β-Benzoyl-α-phenyl-αβ-dibenzylhydrazine, $CHPh\cdot NPh\cdot NBz\cdot CH_2Ph$, crystallises from alcohol, in which it is readily soluble, and has m. p. 107°; the corresponding *acetyl* derivative, $C_{22}H_{22}ON_2$, obtained by boiling the hydrochloride of the base with acetic anhydride, has m. p. 78°.

α-Phenyl-αβ-dibenzylhydrazine hydrochloride does not react with potassium cyanate; when boiled for several hours with 20% hydrochloric acid, it yields benzyl chloride and phenylhydrazine.

Tribenzylhydrazine hydrochloride, $CH_2Ph\cdot NH\cdot N(CH_2Ph)_2,HCl$, obtained by reducing the corresponding benzylidene derivative, or by the action of benzyl chloride on hydrazine hydrate, crystallises from alcohol in compact needles, m. p. 181°. When boiled for fifty-six hours with 20% hydrochloric acid, it yields benzyl chloride and hydrazine hydrochloride.

The product obtained by reducing 1-benzylideneamino-2 : 5-diphenyl-1 : 3 : 4-triazole with sodium amalgam and alcohol is diphenyltriazole (Pinner, *loc. cit.*), the *hydrochloride* of which has m. p. 203°.

The following generalisations with regard to the decomposition of tertiary hydrazines by boiling hydrochloric acid are given: (1) When the substituents are aryl groups, the hydrazine undergoes a benzidine rearrangement if such be possible. Quaternary hydrazines can, in addition, undergo fission at the $\equiv N\cdot N\equiv$ union. (2) When the substituents are partly aromatic and partly aliphatic, several reactions are possible. As a rule, the hydrazine with cold hydrochloric acid is transformed into a primary hydrazine and a hydrazone of the hydrazine. When two aliphatic and one aromatic groups are present, heating with 20% hydrochloric acid leads to the formation of the primary aromatic hydrazine and an alkyl chloride (2 mols.). Quaternary hydrazines with two aromatic and two aliphatic substituents undergo fission at the nitrogen linking. (3) Aliphatic hydrazines, as a rule, yield hydrazine and alkyl chlorides. The decomposition of *as.-sec.*-aliphatic hydrazines and of quaternary aliphatic hydrazines has not been studied. J. J. S.

Structure of the Azoxy-compounds. ANGELO ANGELI and LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 896—900).—*p*-Nitroazoxybenzene prepared by Zinin's method (*Annalen*, 1860, **114**, 218) has m. p. 152° (Zinin: 153°). *p-Nitroazobenzene*, prepared

from nitrosobenzene and *p*-nitroaniline, forms red laminæ, m. p. 135°. Oxidation of this substance with hydrogen peroxide in solution in glacial acetic acid yields a compound, m. p. 148°, which also differs in colour and solubilities from the *p*-nitroazoxybenzene of Zinin. It is suggested that the two substances are isomerides having the formulæ $Ph\cdot NO\colon N\cdot C_6H_4\cdot NO_2$ and $Ph\cdot N\colon NO\cdot C_6H_4\cdot NO_2$ respectively.

R. V. S.

New Synthesis of *o*-Hydroxyazobenzene. N. N. Voroschtsoff (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 787—791).—Although *p*-nitrophenol and *p*-aminophenol do not combine with diazo-salts, *p*-acetylaminophenol readily yields *m*-acetylamino-*o*-hydroxyazobenzene. When treated with concentrated hydrochloric acid, the latter easily loses the elements of acetic acid, yielding *m*-amino-*o*-hydroxyazobenzene hydrochloride. On diazotising this with amyl nitrite in glacial acetic acid solution (compare Hantzsch and Jochem, Abstr., 1902, i, 62), a solid diazo-compound is obtained, which, on treatment with boiling alcohol, gives *o*-hydroxyazobenzene in more than 50% yield (calculated on the aminohydroxyazobenzene hydrochloride). This method of preparing *o*-hydroxyazobenzene hence gives much better results than that of Bamberger (Abstr., 1900, i, 531).

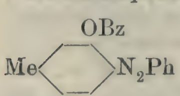
m-*Acetylamino*-o-*hydroxyazobenzene*, $NHAc\cdot C_6H_3(OH)\cdot N_2Ph$, crystallises from acetic acid in long, straw-yellow needles, m. p. 226°.

T. H. P.

Action of Substituted Hydrazines on β-Orthotoluquinone. William McPherson and Cecil Boord (*J. Amer. Chem. Soc.*, 1911, **33**, 1525—1531).—In the case of the reaction between *o*-benzoquinone and *as*-acylphenylhydrazines a migration of the acyl group takes place (compare McPherson and Lucas, Abstr., 1909, i, 193), and the conclusion is drawn that the acyl derivatives of the *o*-hydroxyazo-compounds, like those of the *p*-series, have the acyl group attached to oxygen, and are therefore represented by the formula $NPh\colon N\cdot R\cdot OAcyl$.

3 : 4-Toluquinone is more readily prepared and more stable than *o*-benzoquinone ; it reacts with *as*-benzoylphenylhydrazine, forming 4-benzeneazo-*m*-tolyl benzoate. When saponified it yields 4-benzeneazo-*m*-cresol isomeric with the corresponding *p*-cresol described by Nölting and Kohn (Abstr., 1884, 900). The compound undergoes no change when dissolved in ether containing a small amount of fused potassium hydroxide and heated for some hours, a fact which makes it extremely probable that the acyl group is joined to oxygen.

3 : 4-*Toluquinone* is a reddish-brown solid, non-volatile, and odourless ; it crystallises in clusters of needles, m. p. 70—75° (decomp.). 4-*Benzeneazo*-m-*tolyl benzoate* (annexed formula) forms orange-yellow needles, m. p. 98°. When saponified with concentrated sulphuric acid, 4-*benzeneazo*-m-*cresol* is obtained in thin, red plates, m. p. 122°.



4-*Tolueneazo*-m-*tolyl benzoate* separates in light orange-coloured needles, m. p. 93°.

4-*Tolueneazo*-m-*cresol* crystallises in thin, lathe-shaped, orange-red crystals, m. p. 148°.

E. F. A.

Bisulphite Compounds of Hydroxyazo-colouring Matters. N. N. Voroschtsoff (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 771—786).—The author has investigated the structure of the compounds formed by sodium hydrogen sulphite with the following hydroxyazo-colouring matters: beneneazo-*p*- and -*o*-cresols and benzeneazo-α- and -β-naphthols. It is found that all hydroxyazo-compounds do not react in the ordinary manner with sodium hydrogen sulphite; thus, *p*- and *o*-hydroxyazobenzenes and benzeneazo-*o*- and -*p*-cresols undergo no change on prolonged boiling with aqueous-alcoholic sodium hydrogen sulphite solution, whereas the azo-derivatives of α- and β-naphthol readily react under these conditions, giving crystalline compounds soluble in water. The acetyl derivatives of the two azonaphthols also react with sodium hydrogen sulphite, the compounds obtained yielding, on decomposition with cold dilute ammonia or sodium hydroxide solution, the same hydroxyazo-compounds as are given under similar conditions by the sodium hydrogen sulphite compounds of the non-acetylated azonaphthols; the acetyl groups evidently undergo hydrolysis during the reaction with the sulphite.

The readiness with which these sulphite compounds are decomposed by even dilute alkalis, taken in conjunction with the fact that hydrazobenzene-*N*-sulphonic acid (compare Bucherer and Donnenburg, Abstr., 1910, i, 144) gives azobenzene only when heated with sodium hydroxide, is not in agreement with Spiegel's view (Abstr., 1885, 987) that these compounds are hydrazo-*N*-sulphonic derivatives. Then, too, aminoazo-compounds react with sodium hydrogen sulphite, giving products identical with those formed by the corresponding hydroxyazo-compounds; thus, treatment with sodium hydrogen sulphite and subsequently with ammonia affords a simple means for the quantitative conversion of the aminoazo- to the hydroxyazo-compounds of the naphthalene series.

The author regards the compounds formed by sodium hydrogen sulphite with the hydroxyazophenols of the naphthalene series as salts of sulphurous esters, those formed by the benzeneazonaphthols, for example, having the structure: $NPh\colon N\cdot C_{10}H_6\cdot O\cdot SO_2Na$.

Although the phenols of the naphthalene series can be readily converted into the corresponding amino-compounds by being heated under pressure with ammonia and ammonium sulphite, thus: $R\cdot OH \longrightarrow R\cdot O\cdot SO_2\cdot NH_4 \longrightarrow R\cdot NH_2$, benzeneazo-α-naphthol does not undergo a similar change, the chief product formed under the conditions named being αα-dinaphthylamine-bis-azobenzene,

$$NPh\colon N\cdot C_{10}H_6\cdot NH\cdot C_{10}H_6\cdot N\colon NPh.$$

Sodium benzeneazo-α-naphthyl sulphite, $NPh\colon N\cdot C_{10}H_6\cdot O\cdot SO_2Na$, forms dark yellow needles, and is stable towards cold dilute acids. The corresponding *barium* salt, $C_{32}H_{22}O_6N_4S_2Ba$, forms microscopic, yellow prisms. The yellowish-green copper salt gradually turns brown, free benzeneazo-α-naphthol being developed. The same sodium salt is also obtained from benzeneazo-α-naphthylamine and sodium hydrogen sulphite.

Sodium benzeneazo-β-naphthyl sulphite forms shining, golden-yellow needles. The *barium* salt is yellow, and the characteristic *copper* salt, $C_{32}H_{22}O_6N_4S_2Cu$, forms shining, dark yellow, hexagonal plates.

When benzeneazo-β-naphthol is heated with ammonia and ammonium sulphite in a sealed tube at 150—160°, the sulphite compound formed undergoes quantitative conversion into benzeneazo-β-naphthol. At temperatures exceeding 200°, new basic products are formed. In the case of the α-compound, however, change takes place even at 125°, and increases in extent as the temperature is raised; thus, a mixture of sodium benzeneazo-α-naphthyl sulphite, alcohol, and ammonia, heated to 180—200° for twelve hours, yielded a *compound*, $C_{32}H_{23}N_5$, as a violet powder with metallic lustre, m. p. 280°; with concentrated sulphuric acid it forms a dark green solution, which becomes cinnamon-yellow and then reddish-violet on dilution. It dyes wool and cotton violet-red in a faintly acid bath, and thus possesses the properties of a basic, substantive colouring matter. A mixture of benzeneazo-α-naphthol, ammonium sulphite, and ammonia when heated to 130—140° for four hours gave benzeneazo-α-naphthylamine and a violet compound resembling that described above in its general properties, but differing from it in giving with concentrated sulphuric acid a dark violet-blue solution, changing to a reddish-violet colour on dilution. Analogous products are formed at still lower temperatures. T. H. P.

Hydrazo-compounds. V. Reaction of Hydrazobenzene with Mixed Aldehydes. BERTHOLD RASSOW and FRITZ BURMEISTER (*J. pr. Chem.*, 1911, [ii], **84**, 249—259).—In continuation of previous work (Abstr., 1901, i, 777; 1910, i, 79) the authors have examined the behaviour of hydrazobenzene towards phenylacetaldehyde, cinnamaldehyde, and salicylaldehyde, and find that whilst phenylacetaldehyde and cinnamaldehyde resemble the aliphatic aldehydes in readily condensing with hydrazobenzene, all attempts to effect a condensation with salicylaldehyde proved fruitless.

β-Phenylethylidenebishydrazobenzene, $CH_2Ph\cdot CH(NPh\cdot NHPh)_2$, prepared by the interaction of hydrazobenzene and phenylacetaldehyde in alcoholic solution at the ordinary temperature, crystallises in pale yellow needles, m. p. 93—95°, and is readily hydrolysed by dilute acids.

When equimolecular quantities of hydrazobenzene and cinnamaldehyde are heated together in ethyl-alcoholic solution, they yield *α-(or β)-ethoxy-β-1:2-triphenyl-3-ethylhydrazimethylene*,

$$\begin{matrix}NPh\\|\\NPh\end{matrix}\!\!>CH\cdot C_2H_3Ph\cdot OEt,$$

which crystallises in white, prismatic needles, m. p. 135°. It is considered probable that the first stage in the reaction consists in the formation of $\begin{matrix}NPh\\|\\NPh\end{matrix}\!\!>CH\cdot CH{:}CHPh$, addition of alcohol subsequently taking place at the double linking, but experiments undertaken with the object of preparing this compound by the condensation of hydrazobenzene and cinnamaldehyde in ethereal or benzene solution yielded no definite results. Attempts to determine the position of the ethoxy-group by hydrolysing the ethoxy-compound with dilute sulphuric acid were also unsuccessful.

*α-(or β)-Methoxy-β-*1 : 2-*triphenyl*-3-*ethylhydrazimethylene*, $C_{22}H_{22}ON_2$, prepared in a similar manner from hydrazobenzene and cinnamaldehyde in methyl-alcoholic solution, crystallises in lustrous, white, rhombic leaflets, m. p. 163°. F. B.

Hydrazo-compounds. VI. Methylhydrazobenzene and Methylbenzidine. BERTHOLD RASSOW and KURT BERGER (*J. pr. Chem.*, 1911, [ii], 84, 260—277).—N-*Methylhydrazobenzene*,

$$NMePh\cdot NHPh,$$

is prepared by heating a benzene solution of hydrazobenzene with methyl sulphate for two days in the presence of magnesium oxide; it crystallises in needles or small, rod-shaped prisms, m. p. 75°, and differs from the parent substance in being very stable. When treated with cold strong hydrochloric acid, it yields an intense, dark green solution, from which N-*methylbenzidine*, $NH_2\cdot C_6H_4\cdot C_6H_4\cdot NHMe$, may be isolated in white needles, m. p. 83°. The latter compound is, however, best prepared in the form of its *hydrochloride*,

$$C_{13}H_{14}N_2,2HCl,$$

which crystallises in microscopic leaflets, decomposing at 250—300°, by the action of strong hydrochloric acid on methylhydrazobenzene in alcoholic solution. It yields a *picrate*, $C_{13}H_{14}N_2,C_6H_3O_7N_3$, crystallising in yellow, microscopic needles, which decompose at 167—169°, and a *platinichloride*, $C_{13}H_{16}N_2PtCl_6$. The *diacetyl* derivative,

$$NMeAc\cdot C_6H_4\cdot C_6H_4\cdot NHAc,$$

crystallises from alcohol in white, triangular prisms, m. p. 238°; the *dibenzoyl* derivative, $C_{27}H_{22}O_2N_2$, in microscopic needles, m. p. 231—233°.

Methylbenzidine condenses with salicylaldehyde, yielding *salicylidene-N-methylbenzidine*, $NHMe\cdot C_6H_4\cdot C_6H_4\cdot N\colon CH\cdot C_6H_4\cdot OH$, m. p. 194°, and, when heated with methyl iodide in methyl-alcoholic solution, is converted into tetramethylbenzidine methiodide, m. p. 263° (Michler and Pattinson, Abstr., 1882, 199), from which tetramethylbenzidine is obtained by distillation with soda-lime.

Its hydrochloride reacts with two molecules of nitrous acid to form 4-*methylnitrosoaminodiphenyl*-4′-*diazonium chloride*, which condenses with dimethylaniline, yielding 4-*methylnitrosoaminodiphenyl*-4′-*azo*-p-*dimethylaniline*, $NO\cdot NMe\cdot C_6H_4\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NMe_2$. This crystallises in microscopic leaflets of a golden lustre, decomposing at 243°. It forms a violet *hydrochloride*, and, when boiled with alcoholic hydrogen chloride, is converted into 4-*methylaminodiphenyl*-4′-*azo*-p-*dimethylaniline*, $NHMe\cdot C_6H_4\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NMe_2$, which crystallises in carmine-red needles, m. p. 234°, and forms a *hydrochloride*, $C_{21}H_{24}N_4Cl_2$.

The *azo-dyes* produced by the combination of diazotised *N*-methylbenzidine with β-naphthol-3 : 6-disulphonic acid and α-naphthylamine-5-sulphonic acid are respectively red and brown.

The alcoholic mother liquors from the preparation of *N*-methylbenzidine hydrochloride by the action of hydrochloric acid on *N*-methylhydrazobenzene contain 2-(or 4)*amino*-4′-(or 2′)*methylaminodiphenyl*, $NH_2\cdot C_6H_4\cdot C_6H_4\cdot NHMe$, together with aniline, methyl-

aniline, and dimethylaniline; the formation of the three last-mentioned substances is represented as follows:

$$2NHPh\cdot NMePh = NMe_2Ph + NH_2Ph + NPh\colon NPh.$$
$$2NHPh\cdot NMePh = 2NHMePh + NPh\colon NPh.$$

The base just mentioned is a strongly refractive, viscid, yellow liquid, b. p. 255°/25 mm., which yields a *diacetyl* derivative,

$$NMeAc\cdot C_6H_4\cdot C_6H_4\cdot NHAc,$$

crystallising in rhombic leaflets, m. p. 327°. It condenses with salicylaldehyde in alcoholic solution, yielding the *compound*,

$$OH\cdot C_6H_4\cdot CH(NMe\cdot C_6H_4\cdot C_6H_4\cdot N\colon C_6H_4\cdot OH)_2;$$

this has m. p. 255°, and is hydrolysed by boiling dilute sulphuric acid into its components. F. B.

Heat Coagulation of Proteins. II. The Action of Hot Water on Egg-albumin and the Influence of Acid and Salts on Reaction Velocity. HARRIETTE CHICK and CHARLES JAMES MARTIN (*J. Physiol.*, 1911, 43, 1—27. Compare Abstr., 1910, i, 597).—Heat coagulation consists of (1) the reaction between the protein and hot water (denaturation), and (2) the separation of the altered protein in a particulate form (agglutination); (2) occurs more rapidly than (1), and the experiments mainly are concerned with the latter. Denaturation, if means are taken to prevent change in acidity, is a reaction of the first order. As the protein is precipitated, free acid is progressively removed from the solution. Experiments are described which show that egg-albumin fixes acid in the cold, and give the relative amount of acid fixed to the acidity of the solution; the process is reversible. Determinations of the amount fixed during coagulation and its dependence on (1) total concentration of acid, and (2) on hydrogen-ion concentration are given. Salts (sodium chloride and ammonium sulphate) lower the rate of reaction, and up to a certain concentration the effect varies geometrically as the salt is added arithmetically. For the explanations advanced, the original paper must be consulted. W. D. H.

The Partial Hydrolysis of Proteins. III. Fibrin Proto-albumose. PHŒBUS A. LEVENE, DONALD D. VAN SLYKE, and F. J. BIRCHARD (*J. Biol. Chem.*, 1911, 10, 57—71).—The most striking difference between hetero- and proto-albumose is in the amount of glutamic acid on hydrolysis. The former yields 9·51, and the latter 0·63%. Proto-albumose is also poor in valine as compared with hetero-albumose. Any difference in the yield of hexone bases is insignificant. W. D. H.

Hæmochromogen and the Spectroscopic Differentiation of Carboxyhæmoglobin and Oxyhæmoglobin. FRANZ MICHEL (*Chem. Zeit.*, 1911, 35, 996).—The author finds that the best reducing agent for changing the colouring matter of the blood into hæmochromogen is an alcoholic, alkaline solution of sodium hyposulphite; a cherry-red coloured solution for the investigation of the absorption spectrum is thus readily obtained at the ordinary temperature, whereas the use of other reducing agents necessitates

warming. Heating the red solution so obtained gradually destroys the hæmochromogen spectrum, the solution becoming yellowish-green, but the addition of a few drops of pyridine to the boiling solution restores the spectrum and further heating has no effect. If the solution, after cooling, is then shaken in the air, the spectrum again disappears, but is reproduced on heating once more.

The sodium hyposulphite reagent may also be used to detect small quantities of carboxyhæmoglobin. After the addition of the hyposulphite to the diluted blood, a few drops of pyridine are added. The colour of the solution changes to an intense yellowish-red, and only the oxyhæmoglobin is changed to hæmochromogen in the cold, the spectrum of carboxyhæmoglobin remaining unchanged. On heating, the carboxyhæmoglobin is changed also into hæmochromogen.

T. S. P.

The Cleavage of Nucleins in Relation to Enzymes, with Special Reference to the Formation of Hypoxanthine in the Absence of Adenase. SAMUEL AMBERG and WALTER JONES (*Zeitsch. physiol. Chem.*, 1911, **73**, 407—415).—The work of Levene and Jacobs on the intermediate products of hydrolysis of the nucleic acids have led them to consider that the part of the molecule which contains purine substances may be represented by the following shortened formula:

$$C_5H_4N_5\cdot C_5H_8O_3\cdot O\cdot PO(OH)\cdot O\cdot PO(OH)\cdot O\cdot C_5H_8O_3\cdot C_5H_4ON_5.$$

By splitting off phosphoric acid, two nucleosides, guanosine and adenosine, are obtained; the former consists of guanine and *a*-ribose, and from it free guanine is obtained by hydrolysis with acids. Adenosine consists of adenine and *d*-ribose, and from it free adenine is obtained on hydrolysis. By the action of nitrous acid these two amino-nucleosides are converted into the hydroxy-nucleosides, xanthosine and inosine (hypoxanthosine). Gland extracts produce the same kind of effect by means of enzymes, but different glands act differently; for example, pig's pancreas decomposes nucleic acid with the formation of guanosine, which is not further changed; adenosine, which is simultaneously formed, is changed to inosine as an end product. Pig's liver extract produces from nucleic acid, xanthosine (by deamidation of guanosine), from which xanthine is then formed. The following list of enzymes is given: (1) phosphonuclease, (2) purine nuclease, (3) guanosine-deamidase, (4) adenosine-deamidase, (5) adenase, (6) guanase, (7) xanthosine-hydrolase, (8) inosine-hydrolase, and (9) xantho-oxydase.

The present experiments show that phosphonuclease and purine-nuclease, which respectively split off phosphoric acid and purine bases, are independent enzymes. Dog's liver can split off phosphoric acid from nucleic acid, but cannot split off adenine from the adenosine so formed; no adenine is found among the products, and it would be if it were formed, since the dog's liver contains no adenase to convert it into hypoxanthine. Nevertheless, dog's liver extract splits off hypoxanthine quantitatively from thymus-nucleic acid; this is because the adenosine formed is deamidised to inosine, and this is hydrolytically split so as to yield hypoxanthine. W. D. H.

The Application of the Optical Method to a Study of the Enzymatic Decomposition of Nucleic Acids. Samuel Amberg and Walter Jones (*J. Biol. Chem.*, 1911, 10, 81—87. Compare Pighini, this vol., ii, 236).—Extracts of organs freed from blood produce the same results as those containing blood; their varying activities on nucleic acids are therefore not due to blood or blood-serum. By the optical method no change was observed in the rotation of thymus-nucleic acid under the influence of serum. Yeast-nucleic acid, however, does suffer a diminution in rotatory power, as Pighini stated, but this does not mean liberation of either phosphoric acid or purine bases. Rotation is also lowered as the temperature rises, and returns to its previous value on cooling. Pighini's results must therefore be accepted with caution. W. D. H.

A Method for the Study of Proteoclastic Enzymes. Philip Adolph Kober (*J. Biol. Chem.*, 1911, 10, 9—14).—Amino-acids (six were tested) form copper salts that yield their copper as hydroxide when boiled with a slight excess of alkali. The polypeptides and peptones tested which form copper salts do not yield their copper as hydroxide when treated in the same way. The method is suggested as one for distinguishing the two classes of substances in digests.
W. D. H.

The Mechanism of Proteoclastic Enzymes. Auguste Fernbach and Marcel Schoen (*Compt. rend.*, 1911, 153, 133—136).—A greater proteoclastic action is produced in the presence of monopotassium phosphate than in that of the dipotassium salt by papayotin, pancreatin, and the proteoclastic enzyme of *Tyrothrix tenius*, acting on fibrin, caseinogen, and other proteins. This difference is due mainly to the reactions of the media. When pancreatin is incubated with a solution of potassium or sodium phosphate, an increase in activity is produced. W. J. Y.

The Behaviour of Phenolase towards Acids. Alexis Bach and B. Sbarsky (*Biochem. Zeitsch.*, 1911, 34, 473—480).—The phenolase was prepared from *Lactarius vellerius*, and its action on pyrogallol was determined by estimating quantitatively the purpurogallin formed. This was done by filtering it off from the solution, dissolving it in concentrated sulphuric acid, and titrating the solution thus obtained, after dilution with water, with $0{\cdot}01N$-permanganate solution. In addition to this, the amount of pigment formed, which remains in solution after removing the purpurogallin, was estimated colorimetrically. It was found that the presence of small quantities of acid accelerated the action of phenolase. With increasing quantities of acid, the amount of purpurogallin diminishes, but that of the soluble pigment increases. At the limit at which the purpurogallin formation ceases, however, the amount of soluble pigment commences to diminish. The amount of the toxic dose of acid, however, is so great in comparison with the amount of ferment that there can be no question of the acid merely acting on a manganese or other metallic compound. By varying phenolase concentrations on the same substrate, the toxic

action of the acid is proportional, not to the absolute phenolase content, but to its activity under the given conditions. The authors draw the conclusion that their results do not accord with Bertrand's theory of phenolase action. S. B. S.

Preparation of Pure Invertase. HANS EULER and SIXTEN KULLBERG (*Zeitsch. physiol. Chem.*, 1911, **73**, 335—344).—Invertase prepared by autolysis (O'Sullivan and Tompson, Trans., 1890, **57**, 834) was purified by solution in water and precipitation with an equal volume of alcohol. Invertase is precipitated with colloidal iron only when other impurities, particularly electrolytes, are also present. The most active preparations were obtained by precipitation of the autolysed liquor with lead acetate, removal of the lead as sulphide, and of the protein by rubbing the filtrate with much kaolin; a final precipitation with alcohol gave an invertase of great activity. This contained 4·7% of nitrogen, which was lessened by diffusion to 1·85%. Molecular-weight determinations based on the rate of diffusion gave a value of 27,000. During diffusion about 25% of impurities of lower molecular weight are separated, and the activity of the invertase correspondingly increased. The activity of the purified invertase was directly proportional to the weight used. E. F. A.

Yeast-Gum. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1911, **73**, 314—316. Compare Euler and Fodor, this vol., i, 607).—Polemical. Invertase is perhaps the magnesium salt of an acid containing nitrogen and phosphorus; it is not a protein. A plea is made for the continuance of the term invertin instead of invertase. The suggestion of Euler and Fodor that invertase is a complex carbohydrate related to yeast-gum is negatived; active preparations containing no trace of yeast-gum have been obtained frequently.

E. F. A.

Influence of the Reaction of the Medium on the Activity of Cellase. New Character Distinguishing it from Emulsin. GABRIEL BERTRAND and ARTHUR COMPTON (*Compt. rend.*, 1911, **153**, 360—363. Compare Abstr., 1910, i, 212, 290, 800; this vol., i, 592). —The diastase from sweet almonds capable of hydrolysing cellose functions best in a medium having almost the same reaction as that of the natural preparation, namely, alkaline to methyl-orange and acid to phenolphthalein, corresponding with a concentration in hydrogen ions of $10^{-6 \cdot 3}$. Addition of more that a trace of acid inhibits the diastatic activity. Cellase in this respect differs from emulsin, which shows maximum activity only in solutions alkaline to phenolphthalein.

W. O. W.

Heat Resistant Lipase. N. L. SÖHNGEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 166—170).—The lipase produced by *Bacterium fluorescens liquefaciens*, *B. pyocyaneum*, *B. punctatum*, and *B. liquefaciens albus* is capable of withstanding a temperature of 100° for five minutes without being rendered inactive, whilst that formed by *Bacterium lypolyticum*, *B. Stutzeri*, *B. fluorescens non-liquefaciens*, *Oidium lactis*,

Aspergillus niger, *Penicillium glaucum*, and *Cladosporium butyri* is destroyed at 80°.

The two enzymes also differ in their relation to small quantities of acid; ordinary lipase is inhibited only when the reaction of the medium is *N*/50-acid, whereas the heat resisting lipase is rendered inactive at *N*/100-acid. H. B. H.

The Chemical Occurrences in Milk Curdling by Rennet. Ivar Bang (*Skand. Archiv. Physiol.*, 1911, 25, 105—144).—Rennet converts the caseinogen of milk into casein, and the latter is then united to calcium phosphate to form the curd. In the thirty or forty years since this was established by Hammarsten little or nothing has been added, especially in relation to the intermediate stages in the reaction. After the addition of rennet, milk remains apparently unaltered for minutes or hours, and then, suddenly, coagulation takes place. It is the object of the present research to ascertain what is occurring before the last step, the actual curdling, is seen. Some of the experiments were performed with milk, and some with solutions of caseinogen prepared by Hammarsten's method. Rennet is destroyed by momentary heating to 65°, and milk is not changed at this temperature. By adding rennet fractionally, summation is noted; for example, the coagulation time on adding 0·1 c.c. of rennet to 10 c.c. of milk was eight minutes, and on adding 0·2 c.c. four minutes; if, however, 0·1 c.c. is added, and four minutes later another 0·1 c.c., then clotting occurs two minutes after the second addition. If, however, the milk after the first addition is heated to 65°, no such summation is seen; and if the second dose of rennet is not added until four minutes after the heating and subsequent cooling, the coagulation time is lengthened. Although the milk had not curdled in the interval, it had undergone certain changes, due to the first addition of rennet and to the heating of the mixture. If a caseinogen solution is boiled, cooled, and then rennet and calcium chloride added, the coagulation time is also shortened, especially in experiments in which any suspended calcium carbonate (used in the preparation of the solution) is removed by centrifugalising. The so-called solution of caseinogen prepared by Hammarsten's method is really a solution of caseinogen united to calcium carbonate; rennet alone does not curdle it; the addition of calcium chloride or phosphate is also necessary; the original solution is opalescent, but clears on the addition of a little sodium chloride; but heating after the addition of this salt restores the opalescence, and this is reversible on alternate heating and cooling. At a high temperature caseinogen has therefore a greater affinity for calcium carbonate than for alkali; at a low temperature this is reversed. The actual curdling is due to the formation of a compound between the caseinogen–calcium carbonate and other calcium salts, such as the chloride or phosphate, and the numerous experiments, both with caseinogen solution and milk, show differences in action between the chloride and the phosphate. The suggestion that these latter salts act as activators of the enzyme was examined and negatived. The longer the enzyme has acted previous to the addition of the calcium chloride, the more rapidly does curdling occur after the addition. Rennet does not produce only a

change in the caseinogen of the milk, but has also something to do with the mobilisation of the calcium salts. Further experiments, which are difficult to summarise shortly, lead to the conclusion that calcium chloride by its osmotic pressure inhibits the dissociation of the caseinogen–calcium carbonate–calcium chloride compound, and the undissociated compound is precipitated; an excess of phosphate, on the other hand, inhibits precipitation; calcium phosphate is insoluble in water, and so cannot affect osmotic pressure; it forms an insoluble compound with the caseinogen; the avidity of caseinogen for calcium salts rises with temperature.

Milk itself contains, in addition to caseinogen, other proteins and salts; the lactose is indifferent to curdling phenomena. The salts are alkali chloride, phosphate and carbonate, and calcium citrate. The influence of the salts is discussed at length with numerous experiments. Calcium citrate favours, alkali citrate inhibits, curdling; the former gives up calcium, the latter removes it from the milk. The effect of milk-serum on the process did not give constant results. Crystalline egg-albumin (and serum-albumin to a less degree) inhibits the process, but this is in part due to the alkali used in neutralising the solution. Egg-white and serum act in the same way. Lact-albumin acts similarly, and colostrum, which is very rich in lact-albumin, has a very strong inhibitory action. This action in all cases is not on the activity of the enzyme in changing caseinogen, but on the final act of curdling. Rennet action is thus very complex; the calcium salts of the milk are partitioned between organic and inorganic acids and the various milk proteins; the caseinogen takes up more and more calcium phosphate long before it is united, sufficient to cause precipitation to occur. There are probably several phases in the formation of casein, and several more in the combination of casein with calcium phosphate. It is doubtful whether rennet should be classed with coagulating enzymes, for rennet does not in itself produce curdling, and the final act of curdling is not true coagulation, but is more akin to the precipitation of protein by neutral salts. Casein itself is capable of re-solution, and can be re-curdled with rennet under appropriate conditions.

The nomenclature adopted in the preceding abstract is that usually adopted in this country. In the original German, caseinogen and casein are spoken of respectively as casein and paracasein. W. D. H.

Further Observations on Rennin and Pepsin in the Gastric Juice of the Calf. A. Rakoczy (*Zeitsch. physiol. Chem.*, 1911, 73, 453—458).—This is a continuation of the author's previous work (Abstr., 1910, i, 801), in which he found that milk curdling is produced by two enzymes in the calf's gastric juice, namely, by pepsin, and by a special milk-curdling enzyme, rennin (chymosin). With increase of age, the latter disappears, but there is no ground for believing that there is any difference in the pepsin of animals of varying ages. W. D. H.

Amylases. III. Preparation and Properties of Pancreatic Amylase. Henry C. Sherman and M. D. Schlesinger (*J. Amer. Chem. Soc.*, 1911, 33, 1195—1204. Compare Abstr., 1910, ii, 1012; i, 799).—Having been much hampered in previous work by the

deterioration of amyloclastic power in pancreatin solutions, the authors have examined the influence of different solvents and precipitants on the amyloclastic activity of commercial pancreatin, and find that it is fairly permanent in 50% alcohol, the pancreatic amylase being recovered in active form from the solution by precipitation with strong alcohol or a mixture of alcohol and ether. By a process involving extraction of dry pancreas powder with 50% alcohol, repeated precipitation, and purification by dialysis in 50% alcohol, preparations having diastatic powers up to 3480 on the new scale (Abstr., 1910, i, 799) have been obtained, corresponding with over 5000 on Lintner's scale, and with $D_{30}^{38} = 500{,}000$ on Wohlgemuth's scale. Six independent preparations showed in the dry substance activities of 3310, 3670, 3540, 3570, 3720, and 3320. This agreement indicates that these preparations are substantially alike, and that the process yields a fairly definite result. The product has a composition and the characteristic reactions of a protein closely resembling Osborne's malt diastase.

The pancreatic amylase thus prepared, acting at 40° on soluble starch made by Lintner's method, formed 6000 times its weight of maltose in twenty minutes, and 211,000 times its weight in thirty hours. It digested 400,000 times its weight of starch to the "erythrodextrin stage" in less than twenty-two hours, and to products giving no reaction with iodine in forty-eight hours. C. S.

Catalase. Oskar Loew (*Biochem. Zeitsch.*, 1911, **34**, 354).—A claim for priority in reference to the action of nitrates on, and the detection of, catalase. S. B. S.

Extraction of Zymase. Alexandre Lebedeff (*Bull. Soc. chim.*, 1911, [iv], 9, 744—750).—Reply to Kayser (compare this vol., ii, 640). The author has systematically studied the factors influencing the activity of the zymase preparation, namely, the temperature and the time of fermentation, the condition and kind of yeast, the method of preservation of the juice, etc. The top yeast, called "parisienne," does not give an active juice either by the process of Lebedeff or by that of Buchner. W. G.

Is Zymase a Diastase? Alexandre Lebedeff (*Bull. Soc. chim.*, 1911, [iv], 9, 672—682; *Ann. Inst. Pasteur*, 1911, **25**, 682—684).—From experiments with an extract made by macerating dried yeast for two hours with three volumes of water, the author finds that the zymase contained in it is a typical diastase. The quantity of sugar fermented, however, is nearly proportional to the amount of co-enzyme present, provided that this is not less than 20%. The unusual activity of the extract prepared by the author's method is due to the amount of co-enzyme contained in it. It is suggested that yeast is more active than any of its extracts, not because it contains more zymase, but because as fast as co-enzyme is destroyed during the fermentation, it is produced again by cellular activity. R. V. S.

Organic Chemistry.

Absorption of Hydrocarbon Gases by Non-aqueous Liquids. ALONZO SIMPSON MCDANIEL (*J. Physical Chem.*, 1911, **15**, 587—610).—The absorption of methane, ethane, and ethylene in ten organic liquids has been determined at a series of temperatures lying between 20° and 60°.

The gas burette and Ostwald absorption pipette were water-jacketed, and the temperatures were maintained approximately equal by means of a suitably proportioned resistance coil in each jacket, the two coils being in series. The gas in the burette was saturated with the solvent vapour and measured at the temperature of each absorption experiment, so that no correction for vapour pressure of solvent was necessary. The solvents were boiled under diminished pressure, and precautions were adopted to remove dissolved air, the presence of which introduces considerable errors.

The solvents, in order of increasing absorptive power at 25° for methane, are methyl, amyl, ethyl, *iso*propyl alcohols, benzene, toluene, *m*-xylene, hexane, heptane. With ethane and ethylene the solvents fall into a similar series, which, however, is quite unlike the order of the same solvents for the less soluble gases nitrogen, carbon monoxide, hydrogen, and carbon dioxide.

It is suggested that the solubilities of the hydrocarbon gases are largely influenced by specific chemical relations with the solvents.

The absorption coefficient decreases in all cases as the temperature rises. R. J. C.

Preparation of $\beta\gamma$-Dimethyl-$\Delta^{\alpha\gamma}$-butadiene. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 235311).—A 70% yield of $\beta\gamma$-dimethyl-$\Delta^{\alpha\gamma}$-butadiene can be obtained by heating pinacone or pinacolin at 400° with a dehydrating agent followed by fractional distillation of the products. F. M. G. M.

Action of Di-iodoacetylene on Organic Bases. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1911, **33**, 1598—1601).—Di-iodoacetylene can be prepared in a yield of 80—90% of the theoretical by passing acetylene into a solution of potassium iodide and adding sodium hypochlorite solution drop by drop. On mixing solutions of di-iodoacetylene and triethylamine in ether, the *compound*, $NEt_3,2C_2I_2$, m. p. 115°, separates in feathery needles. Dipropylamine when treated in the same way yields the *compound*, $NHPr_2,2C_2I_2$, m. p. 160°, which forms long needles. By the action of acetylene di-iodide on phenylhydrazine, nitrogen is evolved and iodophenylacetylene is produced, together with two phenylhydrazine *hydriodides*, $2NHPh{\cdot}NH_2,HI$, m. p. 128° (decomp.), and $NHPh{\cdot}NH_2,HI$, which does not melt below 300°. E. G.

Action of Alkaline Solutions on Trichlorinated Organic Compounds. G. BRESSANIN and E. SEGRÈ (*Gazzetta*, 1911, **41**, i, 671—674).—Trichloro*iso*propyl alcohol (Mossler, Abstr., 1908, i, 751), phenyltrichloromethylcarbinol (Jocitsch, *Chem. Zentr.*, 1897, i, 1013), and chloroform (Mossler, *loc. cit.*) yield carbon monoxide when treated with alkalis. The authors find that acetonechloroform behaves similarly, and the amount of carbon monoxide evolved indicates that the substance decomposes chiefly according to the equation

$$CCl_3\cdot CMe_2\cdot OH = COMe_2 + CHCl_3.$$

R. V. S.

Fusibility Curves of Gaseous Mixtures: Oxonium Systems Formed by Acetylene, Ethylene, Nitric Oxide, and Methyl Ether. GEORGES BAUME and ALBERT F. O. GERMANN (*Compt. rend.*, 1911, **153**, 569—572. Compare this vol., i, 414; ii, 696).—The fusibility curve for methyl ether and acetylene shows a very sharp maximum at $-117\cdot4°$, corresponding with the compound $Me_2O\colon C_2H_2$. The existence of an analogous compound with ethylene is evident from the occurrence of a maximum at $-163\cdot2°$, but this is unstable in the liquid phase. The curve for methyl ether and nitric oxide shows a maximum at $-166\cdot3°$, corresponding with an oxonium compound, to which the constitution $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!O\!<\!\!\begin{matrix}NO\\NO\end{matrix}$ is ascribed.

Methyl ether has m. p. $-138\cdot4°$. W. O. W.

Primary Aliphatic Dinitro-, Nitro-nitrite, and Dialdoxime Compounds. JULIUS VON BRAUN and WLADISLAUS SOBECKI (*Ber.*, 1911, **44**, 2526—2534).—It has been shown to be possible to apply V. Meyer's method of preparing nitro-compounds from alkyl halides to dihalogen compounds which contain the halogen atoms at some distance from one another in the molecule. $\alpha\delta$-Dinitrobutane, $\alpha\epsilon$-dinitropentane, and $\alpha\kappa$-dinitrodecane have been isolated and found to be stable substances. The nitro-nitrite compounds are considerably less stable.

On cautious reduction, the dinitro-compounds are converted into dioximes, hence affording a useful method of preparing aliphatic dialdehydes.

$\alpha\delta$-Di-iodobutane was allowed to react in ethereal solution with silver nitrite. From the product three fractions were isolated by distillation.

1. A small quantity of *butyl dinitrite*, $NO\cdot O\cdot[CH_2]_4\cdot O\cdot NO$, b. p. $-105°/15$ mm.

2. *Nitrobutyl nitrite*, $NO_2\cdot[CH_2]_4\cdot O\cdot NO$, b. p. about 110°/14 mm., a liquid of ethereal odour, which soon began to decompose. On treatment with stannous chloride in hydrochloric acid solution, this liquid yielded δ-hydroxybutylamine, b. p. 100°/15 mm. The dibenzoyl derivative of the latter was found to melt at 75°, whereas Henry found 58°.

3. *$\alpha\delta$-Dinitrobutane* is an almost colourless, practically odourless liquid of b. p. 176—178°/13 mm.; the *sodium* salt was analysed. Bromine transformed it into *$\alpha\alpha\delta\delta$-tetrabromo-$\alpha\delta$-dinitrobutane*, $NO_2\cdot CBr_2\cdot CH_2\cdot CH_2\cdot CBr_2\cdot NO_2$, m. p. 100°.

$\alpha\epsilon$-Di-iodopentane and silver nitrite gave a similar series of products. *Nitroamyl nitrite*, b. p. 130—133°/15 mm., was found to be somewhat unstable. Reduction transformed it into *ε-hydroxyamylamine*,

$$OH\cdot[CH_2]_5\cdot NH_2,$$

a colourless liquid, b. p. 122°/16 mm., which forms an oily *benzoyl* derivative and a *gold* salt. The constitution of this compound was proved by its reduction to piperidine by means of fuming hydriodic acid.

αε-Dinitropentane is an almost colourless liquid, b. p. 194—196°/16 mm. Its salts resemble those of αδ-dinitrobutane. The *sodium* salt when treated with benzenediazonium sulphate yields the *compound*, $N_2Ph\cdot CH(NO_2)\cdot[CH_2]_3\cdot CH(NO_2)\cdot N_2Ph$, m. p. 169°. *ααεε-Tetrabromo-αε-dinitropentane* has m. p. 39°.

ακ-Dinitrodecane, $C_{10}H_{20}O_4N_2$, m. p. 49°, was obtained by similar methods. The *tetrabromo*-derivative is an oil.

On reduction with stannous chloride in hydrochloric acid solution, dinitropentane gives glutardialdoxime, m. p. 178° (Harries, Abstr., 1910, i, 361, gives 171°); dinitrobutane gives succindialdoxime, and dinitrodecane furnishes *ακ-dioximinodecane*, m. p. 137—141°.

H. W.

Anhydrous Formic Acid. James B. Garner, Blair Sexton, and H. O. Parker (*Amer. Chem. J.*, 1911, **46**, 236—240).—Attention is drawn to the lack of agreement in the values given by previous investigators for the physical constants of formic acid. The methods of dehydration hitherto employed yield only a 97—98% acid.

The anhydrous acid is best prepared by distilling the ordinary acid over anhydrous copper sulphate under a pressure of 120 mm. It has m. p. 8·35°, b. p. 50°/120 mm., 99·7°/741 mm.

The density and viscosity of the pure acid have been determined at temperatures varying from 10° to 40°: D^{15} 1·2260, D^{20} 1 2200.

F. B.

Soy Bean Oil. Hermann Matthes and A. Dahle (*Arch. Pharm.*, 1911, **249**, 424—435. Compare this vol., i, 858).—The oil contains about 94% of fatty acids in the form of glycerides. The fatty acids comprise palmitic 15%, oleic 56%, linoleic 19%, and linolenic 4·8% approximately (compare Lewkowitsch, *Oils, Fats, and Waxes*, 1909, 2, 124, and Keimatsu, this vol., i, 766).

The two oils examined were "refined" and "unrefined," and gave the following constants respectively: D^{15} 0·9260 and 0·9265; solidifying point −11·5°, −12°; n_D^{40} 1·468, 1·468; $[\alpha]_D$ 0°, 0°; acid number 5·711, 1·713; saponification value 192·3, 194·3; Hehner number 94·07, 95·52; iodine value 131·3, 132·6; Reichert-Meissl value 0·7549, 0·7549; Polensky number 0·7843, 1·0784. Both oils gave the elaidin reaction. The two oils were exposed to (1) damp air, (2) dry air, (3) oxygen, (4) damp oxygen during six months, and then re-examined. The results indicated that (1) moisture raised the acid number; (2) oxygen alone or in presence of moisture did not lower the iodine value, whilst (3) damp air reduced the iodine value from 131·3 to 122·5 and from 132·6 to 105·4 for the refined and unrefined oils respectively.

Farnsteiner's process applied to the mixed fatty acids gave a good separation of palmitic acid, but the mixed unsaturated acids thus obtained still contained some saturated acid. Bremer's method gave a bad separation of saturated acid, but the mixed unsaturated acids obtained contained less palmitic acid than the product obtained by Farnsteiner's method. No separation of components of the mixed unsaturated acids could be effected by fractional distillation, and recourse was had to bromination, and a method is described for the successive separation of linolenic acid hexabromide, linoleic acid tetrabromide, and oleic acid dibromide from the mixture. T. A. H

Preparation and Properties of α-Linolenic Acid from Linseed Oil. ERNST ERDMANN (*Zeitsch. physiol. Chem.*, 1911, **74**, 179—197).—The acids obtained by the hydrolysis of linseed oil are freed from the solid acids at -18° in the presence of petroleum, and the residual liquid acids are converted into their zinc salts by trituration with freshly precipitated basic zinc carbonate. By extracting the salts with alcohol, the easily soluble zinc α-linolenate can be removed, and from it pure α-linolenic acid obtained in 16—18% yield, calculated on the liquid acids. The acid, the purity of which is controlled by its iodine number, 269—278, and by its quantitative conversion into the hexabromide, m. p. 179°, is an unstable, somewhat mobile liquid, D_4^{20} 0·9046 (after a few days, D_4^{21} 0·9248); the *zinc* salt, $(C_{18}H_{29}O_2)_2Zn,\frac{1}{2}ZnO$, m.p. 72—73°, *ammonium*, *barium*, *sodium*, and basic *copper* salts are described. The acid yields *trichlorotri-iodostearic acid*, $C_{18}H_{30}O_2Cl_3I_3$, m. p. 146°, with iodine chloride, and *tribromotri-iodostearic acid*, m. p. 124—126°, with iodine bromide, and is converted by ozone into an *ozonide peroxide*, $C_{18}H_{30}O_{12}$, which is decomposed by cold water, yielding hydrogen peroxide and a semi-solid mass consisting probably of the semialdehyde of azelaic acid and malondialdehyde.

The paper concludes with a reply to Rollett (this vol., i, 175). It is very questionable whether β-linolenic acid is present in linseed oil, although there is no doubt that it constitutes the chief ingredient of the mixture of acids obtained by the debromination of α-linolenic acid hexabromide. C. S.

Keto-enolic Tautomerism. III. Tautomerism of Ethyl Acetoacetate. KURT H. MEYER and PAUL KAPPELMEIER (*Ber.*, 1911, **44**, 2718—2724).—Knorr, Rothe, and Averbeck's general results on the desmotropy of ethyl acetoacetate (this vol., i, 516) confirm those obtained by K. H. Meyer (this vol., i, 350), but these authors found that, in a state of equilibrium, the ester contains 2% of the enolic form, whilst Meyer's results indicated 7·71%.

The authors have therefore investigated the sources of error in Meyer's method, namely, the necessity of adding a slight excess of bromine before a recognisable yellow colour is obtained, the conversion of ketonic into enolic form during the titration, and the possible presence in the alcoholic bromine solution of substances which liberate iodine from potassium iodide (such are really present in old, but not in fresh, solutions); but when allowance is made for all

these errors, the proportion of the enolic form is still found to exceed 7%.

The principal errors may be eliminated by adding to the solution, immediately after the bromine, alcoholic β-naphthol solution, which does not react with iodine, but does so very rapidly with bromine, giving a product unacted on by hydrogen iodide; the solution of the ester in alcohol at $-7°$, and the addition of the alcoholic bromine and β-naphthol solutions need not occupy more than fifteen seconds. The bromide of the ethyl acetate is then estimated by addition of potassium iodide and titration of the separated iodine with thiosulphate. By this method the presence of 7·4% of the enolic form is indicated. The difference between this and Knorr, Rothe, and Averbeck's value hence remains unexplained.

This titration method can only be employed where the bromine is added instantaneously to the ester, and where the transformation of the one form of the ester into the other is not too rapid.

The publication of Piccard's results (this vol., ii, 561) has led the author to apply the above method to the equilibrium of solutions of widely varying concentrations of ethyl acetoacetate in alcohol, benzene, carbon disulphide, and *n*-hexane. The surprising result was obtained that up to dilutions which can still be accurately investigated by the titration method, namely, $N/5$—$N/10$, the proportion of the enolic form present continues to increase with the dilution, the equilibrium hence depending on the concentration. This is explained on the assumption that the solvent itself does not remain constant on dilution, but consists of a variable mixture of alcohol, etc., and the ester. Also, Dimroth (this vol., ii, 31) has shown that the equilibrium is dependent on the solubilities of the two components, and it may be that additicn of the ester increases the solubility of the ketonic form and so increases its proportion.

For the four solvents named above, the curves connecting the logarithm of the concentration with the percentage of enolic compound in the ester apparently become perpendicular to the enolic axis at high dilutions, as though the equilibrium were then independent of the concentration, but the errors of the method are too great with dilute solution to permit of this relation being definitely established.

T. H. P.

Keto-enolic Tautomerism. IV. Ferric Chloride Reaction of Enols. KURT H. MEYER (*Ber.*, 1911, 44, 2725—2729).—No quantitative measurements have been made of the velocity of enol-formation with ethyl acetoacetate, or of the quantity of enol-iron-compound formed with ferric chloride, but from their conductivity measurements Hantzsch and Desch (Abstr., 1902, i, 708) drew the conclusion that only very little enolate is present in an iròn enolate solution of ethyl acetoacetate, in spite of the intensity of the colour. This conclusion is not confirmed by the author's results.

The estimation of enol in ethyl acetoacetate by titration with bromine (this vol., i, 350; preceding abstract) can be effected also in

presence of ferric chloride, the titration being continued until the violet colour of the enolate disappears. As the colour soon returns again, owing to further enolisation, and can then be destroyed again by further addition of bromine water, and so on, the reaction serves as a striking lecture experiment. In order to avoid enolisation during the titration, this must be carried out as rapidly as possible and at 0°.

Varying proportions of aqueous ethyl acetoacetate and ferric chloride solution were mixed, left at 0° for an hour so that equilibrium might be established, and titrated with $N/10$-bromine water. The results show that the ferric chloride exerts a direct enolising action, the quantity of enol formed varying with, but not proportionally to, the amount of ferric chloride added. The law of mass action leads to, the equation: $C_{\text{enolate}} = K.C_{\text{enol}'}.C_{\text{Fe}^{\cdot\cdot\cdot}} = K.C_{\text{Fe}^{\cdot\cdot\cdot}}.C_{\text{ketone}}/C_{\text{H}^{\cdot}}$, the quantity of enolate formed being dependent on the number of hydrogen ions present; indeed, the complex salt can be decomposed and the solution decolorised by addition of acid. With low concentrations of the ferric chloride, its hydrolysis, and hence the free acid present in it, may be neglected, so that it can be assumed that, in a state of equilibrium, the hydrogen ions correspond with the hydrochloric acid liberated from the ferric chloride by the enol. Hence $C_{\text{enolate}} = K\sqrt{C_{\text{FeCl}_3}.C_{\text{ketone}}}$. The values of this expression agree fairly well for low concentrations of ferric chloride, but vary considerably for the higher concentrations. It may be that in the latter case the free acid in the ferric chloride influences the equilibrium, and that with higher enol-concentrations which require larger amounts of bromine solution, the liberated hydrogen bromide destroys some of the enolate.

In alcoholic solution the quantity of enolate cannot be estimated so accurately, owing to the change of colour on titration being less distinct, but the colour of the enolate quickly re-appears, so that the velocity of conversion of keto- to enol-form is apparently catalytically accelerated to a considerable extent.

That the slow formation of enolate is in reality due to the slowness of enolisation is shown by the fact that enolate formation is a unimolecular reaction, its course being quite analogous with that of enolisation by halogens (compare Lapworth, Trans., 1904, 85, 30). The velocity constant, $K = 0{\cdot}017$ at 0°, shows that the catalytic action of ferric chloride is almost exactly as weak as that of free hydrochloric acid (this vol., i, 350). In alcoholic solution ferric chloride exerts a much more marked catalytic effect on enolisation. T. H. P.

Formation of Lævulic Acid from Glucosamine, Chitin, and Chitose. HEDWIG HAMBURGER (*Biochem. Zeitsch.*, 1911, 36, 1—4).—Lævulic and formic acids are produced when *d*-glucosamine and chitin are heated for four or five days with 25—30 per cent. sulphuric acid.

By treatment with sodium nitrite, glucosamine hydrochloride may be converted into chitose, and this when heated with hydrochloric acid also forms lævulic acid. These substances must therefore be included in those groups contained in the protein molecule which yield lævulic acid when hydrolysed with strong mineral acids. W. J. Y.

The Walden Inversion. VII. Optically Active Leucic (α-Hydroxy*iso*hexoic) Acid and its Transformation into α-Bromo*iso*hexoic Acid. HELMUTH SCHEIBLER and ALVIN S. WHEELER (*Ber.*, 1911, **44**, 2684—2690. Compare Abstr., 1911, i).—The resolution of α-hydroxy*iso*hexoic acid into its optically active components has been accomplished by the crystallisation of its quinidine salt.

l-Leucine on treatment with nitrous acid yields *l*-hydroxy*iso*hexoic acid, the ethyl ester of which is converted by the action of bromine and phosphorus into ethyl *d*-α-bromo*iso*hexoate. Since it has been shown by Fischer (Abstr., 1907, i, 194) that the *l*-bromo-ester may be obtained from the *l*-bromo-acid formed by the action of nitrosyl bromide on *l*-leucine, it is, therefore, possible to convert the latter into the ethyl ester of either *d*- or *l*-α-bromo*iso*hexoic acid.

dl-α-Hydroxy*iso*hexoic acid, prepared by the action of aqueous sodium hydroxide on α-bromo*iso*hexoyl bromide, first at the ordinary temperature and then at 100°, crystallises in rhombic plates, m. p. 76—77° (compare Röhmann, Abstr., 1908, i, 56; Gmelin, Abstr., 1893, i, 501); the *ethyl* ester has b. p. 80—81°/16 mm., and yields *ethyl* dl-*α-bromo*iso*hexoate*, b. p. 86—87°/11 mm., when treated with phosphorus and bromine

The resolution of the acid into its optically active components may be effected by means of the quinine or brucine salts, but most readily by crystallisation of the quinidine salt.

l-*α-Hydroxy*iso*hexoic acid* crystallises in thin prisms, m. p. 81—82°, with previous sintering at 78°, and has, in *N*-sodium hydroxide $[\alpha]_D^{20}$ $-27{\cdot}8°$ ($\pm 0{\cdot}2°$), in water $[\alpha]_D^{20}$ $-10{\cdot}4°$ ($\pm 0{\cdot}2°$). It may also be obtained by the action of nitrous acid on *l*-leucine, no appreciable racemisation taking place during the transformation; the *barium* salt was analysed. The d-*isomeride* could not be obtained pure by the crystallisation of its alkaloidal salts, and is, therefore, best prepared from *d*-leucine and nitrous acid; in *N*-sodium hydroxide it has $[\alpha]_D^{20}$ $+2{\cdot}63°$ ($\pm 0{\cdot}2°$).

Ethyl l-*α-hydroxy*iso*hexoate*, prepared by esterifying the *l*-acid with alcohol and hydrogen chloride, has b. p. 79—80°/12 mm., $[\alpha]_D^{20}$ $-11{\cdot}07°$ ($\pm 0{\cdot}02°$), D^{20} 0·965, and is converted by treatment with phosphorus and bromine into ethyl *d*-α-bromo*iso*hexoate, considerable racemisation accompanying the action. F. B.

Lactarinic Acid and Ketostearic Acid Isolated from Fungi of the genus Lactarius. J. BOUGAULT and C. CHARAUX (*Compt. rend.*, 1911, **153**, 572—573*).—Thörner's lactarinic acid has been isolated from *Lactarius theiogalus*, *L. plumbeus*, etc., but does not occur in all species. It is extracted by alcohol, and obtained as spangles, m. p. 87°, having the composition $C_{18}H_{34}O_3$. The substance appears to be a ketonic acid, since it yields an *oxime*, m. p. 59—61°, which undergoes the Beckmann transformation, giving a *compound*, m. p. 104°; the *ethyl* ester has m. p. 41°. Reduction of the acid by means of sodium and alcohol leads to the formation of an *hydroxy-acid*, $C_{18}H_{36}O_3$; this substance yields an *acetyl* derivative, m. p. 52—53°, and furnishes stearic acid when its iodo-derivative is reduced with zinc and acetic acid. W. O. W.

* and *J. Pharm. Chim.*, 1911, [vii], 4, 337–343.

β-Butanolglycuronic Acid. SUMIO SANEYOSHI (*Biochem. Zeitsch.* 1911, **36**, 22—24).—Methyl ethyl ketone when given to rabbits by the mouth undergoes reduction in the body, and is excreted in the urine as a β-butanol derivative of glycuronic acid. This compound was isolated as the barium salt, $C_{10}H_{17}O_7Ba$, and from the fact that it did not reduce Fehling's solution directly, a glucoside formula is attributed to it. W. J. Y.

Action of the Chlorides of Dibasic Fatty Acids on Ethyl Sodioacetoacetate. JOHANNES SCHEIBER [with P. LUNGWITZ] (*Ber.*, 1911, **44**, 2422—2429).—Chlorides of succinic, glutaric, and adipic acids react with ethyl sodioacetoacetate to form compounds of the type $[CH_2]_n[CO{\cdot}CH(COMe){\cdot}CO_2Et]_2$. In addition, succinyl chloride reacts with 1 mol. of ethyl sodium acetoacetate, yielding *ethyl succinylacetoacetate*, $CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH(COMe){\cdot}CO_2Et$. The corresponding malonic ester derivative (Scheiber, Abstr., 1909, i, 363) has a cyclic structure, but the succinyl ester shows no tendency either to form a γ-lactone or other cyclic derivative.

Ethyl succinylacetoacetate crystallises in prisms, m. p. 82°; it gives a red coloration with alcoholic ferric chloride. With phenylhydrazine four products are obtained:

(*a*) The *phenylhydrazine* salt of *ethyl-β-carboxypropionylacetoacetate*-bis-*phenylhydrazone*, m. p. 138°, forming colourless, unstable needles.

(*b*) A *pyrazole*, $C_{16}H_{18}O_4N_2$, the colourless crystals of which have m. p. 43°.

(*c*) A *base*, $C_{14}H_{14}O_2N_2$ or $C_{28}H_{28}O_4N_4$, m. p. 157°.

(*d*) A *product*, m. p. 214—215°, soluble in alcohol.

With hydroxylamine an iso*oxazole*, m. p. 81°, is obtained. With hydrazine the products are a *hydrazone*, m. p. 188°, and a *substance*, m. p. 118°.

Ethyl succinyldiacetoacetate was obtained as an oil; it showed a cornflower-blue coloration with sulphuric acid changing to green.

Ethyl glutaryldiacetoacetate, $CH_2[CH_2{\cdot}CO{\cdot}CH(COMe){\cdot}CO_2Et]_2$, is an oil of acid properties; with phenylhydrazine it gives *glutaric acid*-bis-*phenylhydrazide*, $CH_2[CH_2{\cdot}CO{\cdot}NH{\cdot}NHPh]_2$, which crystallises in plates, m. p. 217—218°.

Ethyl adipyldiacetoacetate is also an oil; with phenylhydrazine, *adipic acid*-bis-*phenylhydrazide*, $C_2H_4(CH_2{\cdot}CO{\cdot}NH{\cdot}NHPh)_2$, is formed; it crystallises in nacreous, lustrous plates, m. p. 206—207°. E. F. A.

Preparation of Additive Compounds of Chloral with Amides. CHEMISCHE FABRIK GEDEON RICHTER (D.R.-P. 234741).—When chloral is fused with a molecular proportion of an acid amide an additive compound is produced.

*Bromo*iso*valeramide-chloral*, $CHMe_2{\cdot}CHBr{\cdot}CO{\cdot}NH_2,CCl_3{\cdot}CHO$, forms small, colourless, odourless crystals with an intensely bitter taste and m. p. 116—118° (decomp.); it is insoluble in petroleum and in water, but dissolves readily in other organic solvents, and is of therapeutic value. F. M. G. M.

Hexose Phosphoric Acid Ester. A. VON LEBEDEFF (*Biochem. Zeitsch.*, 1911, 36, 248—260. Compare Abstr., 1910, i, 716; Young, *ibid.*, 12).—The author gives a short historical sketch of the rôle of phosphoric acid in alcoholic fermentation. A further investigation of the phenyl- and *p*-bromophenyl-hydrazones showed that the derivatives contain one molecule of hexose to two molecules of phosphoric acid, corresponding with Young's suggested formula for the phosphoric acid ester, $C_6H_{10}O_4(RPO_4)_2$. The sodium and lead salts of the osazone of the ester were prepared and analysed, the full experimental method being given, and the formulæ given by the author two years ago were confirmed. The author claims that the possibility of ascribing the correct formula given by Young is due to his own investigations, and the isolation by him of osazones and hydrazones. The paper is very controversial. S. B. S.

Preparation of Phosphoric Acid Esters of Carbohydrates and of Glycerol. CARL NEUBERG and E. KRETSCHMER (*Biochem. Zeitsch.*, 1911, 36, 5—14).—*Calcium* d-*galactophosphate*, $C_6H_{11}O_9PCa,H_2O$, is obtained by slowly adding a solution of phosphoryl chloride in chloroform to a suspension of calcium carbonate in water containing *d*-galactose, which is stirred continuously and cooled in a freezing mixture; it is a white powder, which in solution in water reduces Fehling's solution and is fermented by beer-yeast.

Lævulose, when treated in the same manner, gave a product which consisted of a double salt of *calcium laevulosephosphate* and calcium chloride, from which the latter could not be removed. The compound was obtained, however, by partly hydrolysing calcium sucrose-phosphate by heating for fifteen minutes with dilute hydrochloric acid. It is a white powder, which gives Seliwanoff's reaction for lævulose, reduces Fehling's solution, and is readily fermented by yeast, thus differing from calcium dextrose-phosphate and sucrose-phosphate. It has the composition $C_6H_{11}O_9PCa,H_2O$.

Calcium glycerolphosphate was obtained in a similar manner to the galactophosphate. W. J. Y.

Nature of the So-called Gallisin in Commercial Starch-Syrup. JOS. GATTERBAUER (*Zeitsch. Nahr. Genussm.*, 1911, 22, 265—290).—That portion of commercial starch-syrup which ferments with difficulty and to which the name gallisin has been applied consists of a new carbohydrate, together with a small quantity of maltose; dextrins are not present. This carbohydrate is termed *glucosin* provisionally, and is an isomeride of maltose, yielding only dextrose on hydrolysis. It may be separated from fermented starch-syrup as a viscous syrup, which, by treatment with a mixture of anhydrous alcohol and ether, is converted into a white or yellowish-white powder. Beer-yeast ferments glucosin slowly, whilst yeast-maltase and emulsin convert it into dextrose. Mineral acids and oxalic acid also convert glucosin into dextrose, but with high concentrations of mineral acids the reaction is reversible. The *phenylosazone*, m. p. 97—100°, is soluble in hot water and in alcohol; the p-*nitrophenylosazone*, m. p. 240°, is a red powder, which yields a

blue coloration when treated with sodium hydroxide. Glucosin also yields amorphous esters with benzoyl chloride, *p*-chlorobenzoyl chloride, *m*-nitrobenzoyl chloride, and benzenesulphonyl chloride. Glucosin is formed by the action of acids on dextrose in the manufacture of starch-syrup (compare Abstr., 1905, i, 684). W. P. S.

Viscosity of Cellulose Solutions. HERMANN OST (*Zeitsch. angew. Chem.*, 1911, **24**, 1892—1896).—A number of determinations of the viscosity of cuprammonium solutions of various forms of cellulose, such as cotton, wood-pulp, cotton-wool, filter paper, &c., have led the author to the conclusion that these viscosity determinations supply useful information on the nature and technical value of celluloses.

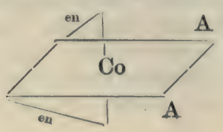
The cuprammonium solution employed was prepared by treating a solution containing 59 grams of copper sulphate with ammonium hydroxide and dissolving the basic copper sulphate thus obtained in ammonium hydroxide (D 0·900) to form one litre of solution. A quantity of cellulose was dissolved in this solution in each case so as to give a solution containing one gram of the anhydrous cellulose in 50 c.c. The viscosity was determined by means of a special form of Ostwald's capillary viscometer.

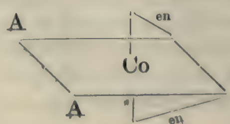
It is found that previous treatment of the cellulose with bleaching agents produces a marked decrease in the viscosity of the cuprammonium cellulose solution; the same result is brought about also by heating the cellulose for about fifteen hours at 120—125°. On the other hand, treatment of the cellulose with a cold 5% solution of sodium hydroxide for about twenty-four hours, or with a cold 20% solution for one hour, does not affect the viscosity of the solution, from which observation the conclusion is drawn that cotton does not undergo a chemical change during mercerisation. Sodium hydroxide, however, does act on cotton chemically, although very slowly, for cotton which has been soaked in a 20% solution of sodium hydroxide, pressed, and kept in a stoppered bottle for several months, dissolves very readily in a cuprammonium solution and forms a solution having a low viscosity.

Cuprammonium solutions of hydrocellulose, obtained by the action of dilute mineral acids on cellulose, are far less viscid than equivalent solutions of cellulose which have been acted on by bleaching agents.

W. H. G.

The Asymmetric Cobalt Atom. II. ALFRED WERNER (*Ber.*, 1911, **44**, 2445—2455).—The author finds that compounds with complex radicles $[A_2 Co en_2]$, in which the two groups A are in the *cis*-position with respect to each other, can be resolved into their optically active isomerides, which is in accordance with the space formulæ of such compounds:





This case is quite different from that reported in the previous communication (this vol., i, 613). Compounds of the type $\left[\begin{matrix}A\\B\end{matrix}\,\mathrm{Co\,en_2}\right]$ contain two tetrahedra, with four different groups (Co, A, B, and en), which are not mirror images of each other, since the ethylenediamine groups possess a different orientation in space in the two tetrahedra, the one being in the same plane as A, and the other in the same plane as B. This is no longer the case with compounds of the type $[A_2\,\mathrm{Co\,en_2}]$, so that they cannot be said to contain an asymmetric cobalt atom; the image and mirror image do not contain a plane of symmetry, but there occurs a kind of molecular asymmetry which the author denotes as *Molecular Asymmetry I.* It is of a simpler character than that occurring with carbon compounds, since there are only two groups, ethylenediamine and A, attached to the cobalt atom.

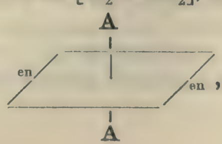
The compounds which have been resolved belong to the 1 : 2-dinitrodiethylenediamine series (the flavo-series), $\left[\begin{matrix}(1)\ O_2N\\(2)\ O_2N\end{matrix}\,\mathrm{Co\,en_2}\right]$, and in the course of their resolution, interesting analogies have been found with carbon compounds. When *d*-camphorsulphonic acid is used, the salt of the *l*-dinitrodiethylenediamine cobalt radicle is difficultly soluble, whilst that of the *d*-radicle is easily soluble. When *d*-bromocamphorsulphonic acid is used, the least soluble salt is that formed with the *d*-radicle. These relations are just the reverse of those which occur in the resolution of optically active carbon compounds, as, for example, in the resolution of tetrahydroquinaldine.

The active 1 : 2-dinitrodiethylenediaminecobalti-salts show a very pronounced anomalous rotation dispersion, the *D*-line being strongly rotated, whereas the *C*-line is rotated to a very small extent or not at all. In 1% solutions the following rotations were observed:

	$[\alpha]_D$.	$[M]_D$.		$[\alpha]_D$.	$[M]_D$.
Chloride	+49° −50	±153°	Bromide	+42·5° −44·0	±151°
Iodide	+34 −35	±139	Nitrate	+41·5 −41·5	±136
Perchlorate	+39 −39·5	±144	Sulphate	+45 −45	±143
d-Flavo-*d* bromo-camphorsulphonate	+66	+383·5	*l*-Flavo-*d*-camphor-sulphonate	−16	−80·32

Very great differences exist in the solubilities of the active and inactive salts, as shown by the following table, where the solubilities are expressed in terms of grams of salt in 100 c.c. of water:

Salt.	Temperature.	*d*-Isomeride.	*l*-Isomeride.	Racemate.	1 : 6-Dinitro-salts.
Nitrate	22°	4·36	4·17	1·2	2·202
Iodide	22	0·49	0·46	0·56	2·652
Sulphate	28	1·63	1·71	2·55	—

Compounds of the formula $[A_2\,\mathrm{Co\,en_2}]$, in which the A-radicles are in the *trans*-position,  should not show optical

isomerism, and in proof of this it was not found possible to resolve the salts of the 1 : 6-dinitrodiethylenediaminecobalti-series (croceo-series).

The cases of isomerism which have been proved to exist in the diacido-diethylenediaminecobalti-salts may be summarised as follows :

(1) *Cis-trans*-isomerism :

$$\left[\begin{matrix}(1)\ O_2N \\ (2)\ O_2N\end{matrix}\ Co\ en_2\right]X \quad \text{and} \quad \left[\begin{matrix}(1)\ O_2N \\ (6)\ O_2N\end{matrix}\ Co\ en_2\right]X.$$

Flavo-salts. Croceo-salts.

(2) Salt isomerism :

$$\left[\begin{matrix}(1)\ ON{\cdot}O \\ (2)\ ON{\cdot}O\end{matrix}\ Co\ en_2\right]X \quad \text{and} \quad \left[\begin{matrix}(1)\ O_2N \\ (2)\ O_2N\end{matrix}\ Co\ en_2\right]X,$$

1 : 2-Dinitritodiethylenediaminecobalt salts. Flavo-salts.

and also the 1 : 6-dinitritodiethylenediaminecobalt salts and the croceo-salts.

(3) Ionisation metamerism :

$$\left[\begin{matrix}O_2N \\ O_2N\end{matrix}\ Co\ en_2\right]X \quad \text{and} \quad \left[\begin{matrix}O_2N \\ X\end{matrix}\ Co\ en_2\right]NO_2.$$

X can be either Cl, Br, or SCN, etc.

(4) Co-ordination polymerism :

$$\left[\begin{matrix}O_2N \\ O_2N\end{matrix}\ Co\ en_2\right]_3\left[Co(NO_2)_6\right] \quad \text{and} \quad \left[Co\ en_3\right]\left[Co(NO_2)_6\right].$$

(5) Mirror image isomerism :

$$d\text{- and } l\text{-}\left[\begin{matrix}(1)O_2N \\ (2)O_2N\end{matrix}\ Co\ en_2\right]X.$$

The inactive 1 : 2-dinitrodiethylenediaminecobalt salts (compare Abstr., 1901, i, 511) are best obtained by heating together 20 grams of potassium cobaltinitrite and 48 grams of 10% ethylenediamine until the mixture begins to froth. The dark brown solution is filtered from unchanged cobaltinitrite, and on keeping deposits brownish-yellow crystals of the 1 : 2-dinitronitrite. The mother liquor, on evaporating, gives at first a further quantity of the salt, and then a mixture of the 1 : 2- and 1 : 6-dinitro-salts which can be separated by fractional crystallisation. The iodide is obtained by heating the hot solution with sodium iodide.

In the resolution of the iodide by means of silver *d*-camphorsulphonate, a precipitate of a mixture of silver iodide and *l*-1 : 2-dinitrodiethylenediaminecobalt *d*-camphorsulphonate is first obtained from the hot solution, from which mixture the camphorsulphonate may be extracted with hot water. The mother liquor from the mixture deposits a partial racemate on cooling, from which further quantities of the *l*-salt can be obtained by appropriate treatment (recrystallisation, etc.). When about 20 grams of the *l*-salt have been obtained, the mother liquors are united, the iodide precipitated, and then treated with silver *d*-bromocamphorsulphonate. After collecting the silver iodide, the hot solution, on cooling, deposits brown needles of *d*-dinitrodiethylenediaminecobalt *d*-bromocamphorsulphonate.

To prepare the various active salts, the camphor- and bromocamphor-sulphonates were precipitated with excess of sodium iodide, the aqueous suspension of the iodide transformed into the base by shaking with silver oxide, and the salts then obtained by neutralisation of the base with the respective acids.

1 : 2-d- and l-*Dinitrodiethylenediaminecobalt chlorides*, YCl, where $Y = \left[\begin{matrix}(1)\ O_2N \\ (2)\ O_2N\end{matrix}\ Co\ en_2\right]$, form brownish-yellow, columnar crystals. The racemate is deep brown in colour, and crystallises in broad, thick plates. The *bromides*, YBr, are similar in colour and shape to the chlorides. The *active iodides*, YI, give well-developed octahedral crystals, whereas the inactive salt is microcrystalline and of prismatic habit. The *active nitrates*, YNO_3, form stout, prismatic or columnar crystals, as distinguished from the long prisms of the inactive compound. The *active sulphates*, Y_2SO_4, give flat prisms or tablets, whilst the inactive salt forms long, silky, light yellow crystals. The *active perchlorates*, $YClO_4$, crystallise in aggregates of short, stout prisms or tablets, whilst the *inactive* salt gives rhombic leaflets of amber-yellow colour.

l-1 : 2-*Dinitrodiethylenediaminecobalt* d-*camphorsulphonate*,

$$Y(O_3S{\cdot}C_{10}H_{15}O),$$

forms long, flat, pointed, golden-yellow crystals. d-1 : 2-*Dinitrodiethylenediaminecobalt* d-*bromocamphorsulphonate*, $Y(O_3S{\cdot}C_{10}H_{14}OBr)$, gives flat, centimetre-long, brownish-yellow prisms. 1 : 6-*Dinitrodiethylenediaminecobalt* d-*camphorsulphonate*,

$$\left[\begin{matrix}(1)\ O_2N \\ (6)\ O_2N\end{matrix}\ Co\ en_2\right][O_3S{\cdot}C_{10}H_{15}O],$$

forms stout, amber-yellow or brownish-yellow prisms, which are often a centimetre long; $[M]_D + 45{\cdot}2$—$47{\cdot}7°$. T. S. P.

Preparation of Mercury Derivatives of Alkali Alkyldithiocarbamic Acetates. Les Etablissements Poulenc Frères and Ernest Fourneau (D.R.-P. 235356. Compare Abstr., 1907, i, 594).—*Ethyldithiocarbaminoacetate*,

$$CO_2Et{\cdot}CH_2{\cdot}NMe{\cdot}CS{\cdot}S{\cdot}NHMe{\cdot}CH_2{\cdot}CO_2Et,$$

leaflets, m. p. 70—71°, is prepared by slowly treating a cooled solution of ethyl methylaminoacetate, $CO_2Et{\cdot}CH_2{\cdot}NHMe$ (60 parts), in anhydrous ether with carbon disulphide (25 parts) in the same solvent. An energetic reaction takes place; an oil separates which rapidly solidifies, and is purified by crystallisation from ether or acetone. The *mercury* salt, $(CO_2Et{\cdot}CH_2{\cdot}NMe{\cdot}CS{\cdot}S)_2Hg$, a pale yellow powder, is obtained when the foregoing compound is treated with a saturated solution of mercuric chloride, and this, when slowly treated with a 30% solution of sodium hydroxide (containing 2 mols. NaOH), yields a bulky, yellow precipitate of the *mercury sodium* double salt,

$$(CO_2Na{\cdot}CH_2{\cdot}NMe{\cdot}CS{\cdot}S)_2Hg,$$

which is isolated in the form of a yellow powder. If the solution of the mercury sodium salt be heated until it darkens, a *compound*, $CO_2Na{\cdot}CH_2{\cdot}NMe{\cdot}CS{\cdot}S{\cdot}Hg{\cdot}S{\cdot}CH_2{\cdot}CO_2Na$, is obtained as a green powder. F. M. G. M.

Preparation of Optically Active Polypeptides from Racemic Compounds. EMIL ABDERHALDEN and HEINRICH GEDDERT (*Zeitsch. physiol. Chem.*, 1911, **74**, 394—408).—As a general rule, digestive ferments only hydrolyse those polypeptides which are built up from amino-acids which occur naturally. An exception is afforded by *d*-leucyl-*l*-tryptophan, which, according to Hans Fischer (Abstr., 1910, i, 22, 599), is hydrolysed by the liver and by pancreatin. Abderhalden and Schuler (Abstr., 1910, i, 304) have pointed out the possibility of racemisation in the preparation of an optically active dipeptide, and consider the hydrolysis observed by Fischer to be due to *l*-leucyl-*l*-tryptophan. The action of pressed yeast juice towards *d*-, *l*-, and *dl*-leucyl-*l*-tryptophan indicates that only *l*-leucyl-*l*-tryptophan is hydrolysed by the enzyme; the racemic compound yields a mixture of *l*-leucine, *l*-tryptophan, and *d*-leucyltryptophan; *d*-leucyl-*l*-tryptophan when pure is not attacked.

It is possible by means of enzymes to obtain optically pure polypeptides from racemic compounds; these are the opposite of the natural compounds, but a comparison of the magnitude of the rotatory power is possible.

Prepared by the action of yeast juice in this manner, *d*-leucylglycine has $[\alpha]_D^{20}$ $-87{\cdot}87°$ to $-88{\cdot}5°$, and glycyl-*d*-leucine, $[\alpha]_D^{20}$ $+37{\cdot}62°$ to $+37{\cdot}1°$, in both cases somewhat higher values than those obtained by Fischer for the optical antipodes. E. F. A.

Remarks on Henze's Paper on the History of Iodogorgonic Acid. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, **74**, 290—300. Compare this vol., i, 617).—Certain misstatements contained in Henze's paper are corrected. W. D. H.

Methylated Guanidines. MARTIN SCHENCK (*Arch. Pharm.*, 1911, **249**, 463—480. Compare Abstr., 1910, i, 99, 545, 546).—The first part of this paper describes attempts to prepare *a*-methylguanidine, $NMe:C(NH_2)_2$, the second, efforts to obtain *aβ*-dimethylguanidine, $NMe:C(NH_2)\cdot NHMe$, and the third gives an account of the preparation of some new methylated guanidines and substances related thereto. The failure to obtain *a*-methyl- and *aβ*-dimethyl-guanidines is due to the tendency these substances have to transform immediately into *β*-methyl- and *s*-dimethyl-guanidines respectively.

By the interaction of thiocarbamide and methylamine in presence of mercuric oxide, *β*-methylguanidine and dicyanodiamide are formed, the first probably by the action of cyanamide, first formed on methylamine. Ethyl iminocarbonate furnishes with methylamine, *ββ'*-dimethylguanidine; with dimethylamine, *as*-dimethylthiocarbamide (*aurichloride*, $B_2,HAuCl_4$, m. p. 105°; platinichloride, $B_2,H_2PtCl_6,2H_2O$, m. p. 115°, anhydrous), and with ammonia, guanidine. Ethyl iminocarbonate appears to undergo methylation when left fourteen days in the cold with methyl iodide and potassium hydroxide solution, since the product reacts with methylamine to form *aββ'*-trimethylguanidine, with dimethylamine to form a substance giving a crystalline aurichloride, $C_{15}H_{80}O_2N_{10}Au_2Cl_8$, m. p. 250—252°, and with ammonia in alcohol to form *β*-methylguanidine (?). With ammonia in one case a small

amount of guanidine was obtained, indicating the presence of unmethylated ester in the material used. Ethyl methyliminodithiocarbonate, $NMe{:}C(SMe)_2$, gives with methylamine in alcohol, $\alpha\beta\beta'$-trimethylguanidine, with ammonia in alcohol, β-methylguanidine, and with dimethylamine a substance yielding a crystalline aurichloride, which melted below 100°.

For the preparation of $\alpha\beta$-dimethylguanidine, $NMe{:}C(NHMe)\cdot NH_2$, the following methods were tried unsuccessfully: Dimethylthiocarbamide treated with ammonia in alcohol in presence of mercuric oxide gave chiefly $\alpha\beta\beta'$-trimethylguanidine with some $\beta\beta'$-dimethylguanidine (compare Chancel, Abstr., 1893, i, 297). *Dimethylethyl-ψ-thiocarbamide*, $NMe{:}C(NHMe)\cdot SEt$, in the form of its *ethiodide*, m. p. 100° (approx.), gives with ammonia in alcohol $\beta\beta'$-dimethylguanidine (compare Noah, Abstr., 1890, 1241), and the same substance was obtained by the action of ammonia on $\alpha\beta\beta'$-trimethyl-ψ-thiocarbamide.

ββ'-Trimethylguanidine aurichloride, $NH{:}C(NHMe)\cdot NMe_2,HAuCl_4$, m. p. 153°, obtained by the addition of gold chloride to the product resulting from the interaction of methylthiocarbamide methiodide (m. p. 135—136°) and dimethylamine in alcohol, forms small needles, and is easily soluble in water.

ββ'-Dimethylthiocarbamide methiodide, m. p. 210—212°, obtained by direct combination of its two components in alcohol, gives an *aurichloride*, $CS(NHMe)_2,CH_3Cl,AuCl_3$, m. p. 122° (approx.), on treatment first with silver chloride and then with gold chloride. The similarly constituted *platinichloride* has m. p. 192—194°. The methiodide reacts with methylamine in alcohol to form $\alpha\beta\beta'$-trimethylguanidine, which is also obtained by the action of methylamine on the corresponding ethiodide. The free trimethyl-ψ-thiocarbamide regenerated from the methiodide gives with ammonia in alcohol, as stated above, $\beta\beta'$-dimethylguanidine, and with dimethylamine, $\alpha\beta\beta\beta'$-tetramethylguanidine, of which the *aurichloride* has m.p. 117° (approx.). T. A. H.

Melamazine from Hydrazine Salt and Dicyanodiamide. KARL A. HOFMANN and OSKAR EHRHART (*Ber.*, 1911, 44, 2713—2717).—Aminoguanidine nitrate may be easily and cheaply prepared from "Nitrolime" (50% calcium cyanamide) and hydrazine sulphate.

When heated with hydrazine or one of its salts, dicyanodiamide (cyanoguanidine) yields a series of hydrazine derivatives, among them a *melamazine*, $(C_3N_3NH_2)_2(NH\cdot NH)_2,H_2O$, distinguished by its ability to take up oxygen in alkaline solution, giving an intensely bluish-violet colouring matter. The *hydrochloride*, $C_6H_8N_{12},HCl$, dissolves in hot water, giving a colloidal solution. The azine exhibits only slight salt-forming capacity, as water effects partial hydrolysis and ammonia liberates the base. It is very stable towards strong acids; when heated with fuming hydrochloric acid for twenty-four hours at 170°, it is largely converted into carbon dioxide, ammonium chloride, and hydrazine hydrochloride, whilst with fuming sulphuric acid at 190° it is slowly decomposed, giving principally ammelide (melanurenic acid). Nitro-hydrochloric acid also attacks it slowly, giving ammeline nitrate. With excess of alkaline permanganate solution, it yields four

atoms of nitrogen per molecule, and, if the reaction is carried to an end on the water-bath, the hydrazine groups are burnt away, whilst the cyanamide part of the molecule loses part of its ammonia and yields substances of the ammeline-ammelide group.

The bluish-violet coloration formed when an alkaline solution of the azine is left exposed to the air is visible even after dilution with 100,000 parts of water. Reducing agents, such as hydroxylamine, hydrazine, hyposulphite, and zinc dust, decolorise the solution instantly, but the colour soon returns in the air. On acidification, the violet alkaline solution becomes wine-red and then colourless, with separation of transparent, flocculent matter.

The colouring matter can be fixed on unmordanted cotton by soaking the tissue with the alkaline solution and then adding calcium chloride solution; the violet colour is changed to red by acids, even by acetic acid. The colouring matter was isolated as *barium* salt, $(C_6HO_2N_{10})_2Ba$, in the form of an opaque, violet-black powder with bronzy lustre; the *thallium* salt, $(C_6O_2N_{10})Tl_3H$, was also prepared.

In concentrated sulphuric acid melamazine gives with a nitrite or nitrate an intense yellowish-red coloration, which resembles the brucine reaction, and on warming turns to blue and then disappears with evolution of gas. Hydrogen peroxide in concentrated sulphuric acid also gives a transitory reddish-yellow coloration, whilst chromic acid yields a deep reddish-brown colour, changing to green, with evolution of gas, on heating. T. H. P.

Prussian Blue and Turnbull's Blue. III. ERICH MÜLLER [and, in part, G. WEGELIN, FREDERICK P. TREADWELL, and OTTO DIEFENTHALER] (*J. pr. Chem.*, 1911, [ii], 84, 353—369. Compare Abstr., 1909, i, 142, 705).—The composition of the precipitates obtained by mixing (0·1 molar) solutions of hydroferrocyanic acid and ferric chloride and of hydroferricyanic acid and ferrous chloride has been investigated by methods similar to those already described. The experiments on the composition of the precipitates formed from potassium ferrocyanide and ferric chloride and from potassium ferricyanide and ferrous chloride have been repeated, with results differing somewhat from those previously given.

The precipitates obtained by mixing potassium ferrocyanide and ferric chloride consist of $Fe_4'''[Fe(CN)_6]_3''''$ only when the ratio $K_4[Fe(CN)_6]/FeCl_3(=x)<0·75$. When x lies between 0·75 and 0·92 the precipitate consists of a mixture of $Fe_4'''[Fe(CN)_6]_3''''$ and $KFe'''[Fe(CN)_6]''''$, whilst as x becomes greater than 0·92, a mixture of these compounds with gradually increasing amounts of $K_2Fe''[Fe(CN)_6]''''$ is produced.

With hydroferrocyanic acid and ferric chloride, when the ratio $H_4[Fe(CN)_6]''''/FeCl_3(=y)<0·75$, the precipitate has the composition $Fe_4'''[Fe(CN)_6]_3''''$. For values of y between 0·75 and 0·85, the precipitate consists of the latter compound mixed with $HFe'''[Fe(CN)_6]''''$. When $y>0·85$ the precipitate consists of a mixture of these two compounds with $Fe_2''[Fe(CN)_6]''''$.

In the case of potassium ferricyanide and ferrous chloride, when the ratio $H_3[Fe(CN)_6]'''/FeCl_2\,(=z)<0·714$, $KFe_2''Fe_5'''[Fe(CN)_6]_5''''$ is

produced. For values of z lying between 0·714 and 0·75, this is accompanied by $KFe''Fe_3'''[Fe(CN)_6]_3''''$. When z varies from 0·75 to 0·9, the precipitate consists of a mixture of $KFeFe_3'''[Fe(CN)_6]_3''''$ and $KFe'''[Fe(CN)_6]''''$, whilst for values of $z > 0·9$, the two latter compounds are accompanied by $Fe_4'''[Fe(CN)_6]''''$, produced according to the equation: $4KFe'''[Fe(CN)_6]'''' = Fe_4'''[Fe(CN)_6]'''' + K_4[Fe(CN)_6]''''$.

Similar results were obtained in the case of ferrous chloride and hydroferricyanic acid. When the ratio $H_3[Fe(CN)_6]'''/FeCl_2 < 0·75$, the precipitate consists of a mixture of $HFe_2''Fe_5'''[Fe(CN)_6]_5''''$ and $HFe''Fe_3'''[Fe(CN)_6]_3''''$; if the ratio $> 0·78$, a mixture of the latter compound with $HFe'''[Fe(CN)_6]''''$ and $Fe_4'''[Fe(CN)_6]_3''''$ is produced.

F. B.

Oxidation of Hydrazine. VI. Reaction between Mercuric Oxide and Hydrazine Hydrate in Alcoholic Solution. C. F. Hale and V. E. Nunez (*J. Amer. Chem. Soc.*, 1911, 33, 1555—1563).—Browne and Shetterly (Abstr., 1909, ii, 658) have shown that when an aqueous solution of hydrazine sulphate is heated with either yellow or red mercuric oxide, neither ammonia nor azoimide is produced, but that if the yellow oxide is added gradually to a slightly alkaline solution of the salt at 0°, both ammonia and azoimide are formed in appreciable quantities.

A study has now been made of the action of mercuric oxide on an alcoholic solution of hydrazine hydrate, and it has been found that at the ordinary temperature the reaction proceeds in accordance with the equation $N_2H_4,H_2O + 2HgO = N_2 + 2Hg + 3H_2O$. The amount of nitrogen actually obtained was slightly less than that required by this equation. Neither ammonia nor azoimide was produced, but indications were obtained of the formation of ethylideneazine. Mercury diethyl was also found to be a product of the reaction, together with a white, waxy, solid compound containing carbon, hydrogen, and about 55% of mercury. The latter substance has a strong odour, resembling that of garlic, does not show a definite m. p., and when applied to the skin produces painful and slow-healing burns. The same compound is slowly produced by the action of diffused daylight on mercury diethyl.

E. G.

The Constitution of Aliphatic Diazo-compounds and of Azoimide. Johannes Thiele (*Ber.*, 1911, 44, 2522—2525).—A theoretical paper in which arguments are brought forward in favour of a hydrazone formula for certain products of the action of hydrazine on ketones and of the formula $HN\colon N\colon N$ for azoimide.

H. W.

Tetra-alkylsilicanes. Artur Bygdén (*Ber.*, 1911, 44, 2640—2652).—A thorough examination of the action of magnesium alkyl halides on silicon tetrachloride shows that the mono-alkyl derivatives, $SiRCl_3$ (where R is ethyl, propyl, butyl, *iso*butyl, or *iso*amyl), and tetra-alkylsilicanes are obtained with comparative ease, but the separation of the dialkyl and trialkyl derivatives presents great difficulties, and these substances have not been obtained pure. Magnesium methyl bromide is a more efficient reagent than the iodide, and by its means tetramethylsilicane, b. p. 26—27°, is easily obtained.

The following substances have been prepared by the usual Grignard reaction; the desired product is finally separated from its ethereal solution by treatment with concentrated sulphuric acid, in which the ether (and usually a small quantity of unexamined silicon derivatives) dissolves, leaving the desired product, which is removed by distillation. *Trimethylpropylsilicane*, $SiMe_3Pr$, b. p. 89·5° (corr.), D_4^{15} 0·7063, from trichloropropylsilicane and magnesium methyl bromide (3·3 mols.); *dimethyldiethylsilicane*, $SiMe_2Et_2$, b. p. 95·8° (corr.), D_4^{15} 0·7214, from dichlorodiethylsilicane and magnesium methyl iodide (2·5 mols.); *trimethylbutylsilicane*, b. p. 115·1° (corr.), D_4^{15} 0·7227, from trichlorobutylsilicane and magnesium methyl bromide (3·2 mols.); *dimethylethylpropylsilicane*, b. p. 121·0° (corr.), D_4^{15} 0·7347, from dichloroethylpropylsilicane and magnesium methyl bromide (2·3 mols.); *trimethyl*iso*amylsilicane*, b. p. 131·5° (corr.), D_4^{15} 0·7322, from trichloro*iso*amylsilicane and magnesium methyl bromide (3·2 mols.); *dimethylethyl*iso*butylsilicane*, b. p. 138·0° (corr.), D_4^{15} 0·7463, from dichloroethyl*iso*butylsilicane and magnesium methyl bromide (2·3 mols.).

Tetra-ethylsilicane has b. p. 153·0° (corr.), and D_4^{15} 0·7694.

The preceding tetra-alkylsilicanes have an odour of petroleum, are almost unattacked by concentrated sulphuric acid or alkalis, are oxidised by concentrated nitric acid at a high temperature, react with chlorine in the cold and with bromine by warming, and explode when their mixture with air or oxygen is heated. The b. p. is lower and the molecular volume (of isomerides) is greater, the larger is the number of methyl groups directly attached to the silicon atom.

The new chlorosilicanes required in the preceding syntheses are: *trichlorobutylsilicane*, $C_4H_9\cdot SiCl_3$, b. p. 148·5—149·5°, D_4^{15} 1·169, from magnesium butyl bromide and silicon tetrachloride; *trichloro*iso*butylsilicane*, b. p. 138—143°, D_4^{15} 1·161, prepared like the preceding compound; *dichloroethylpropylsilicane*, b. p. 152—158°, D_4^{15} 1·048, from trichloropropylsilicane and magnesium ethyl bromide; *dichloroethyl*iso*butylsilicane*, b. p. 165—174°, from trichloro*iso*butylsilicane and magnesium ethyl bromide. C. S.

Organo-metallic Ester Compounds. I. Iodostanni-ester Compounds. BRUNO EMMERT and WILHELM ELLER (*Ber.*, 1911, 44, 2328—2330).—Tin reacts with ethyl iodoacetate in presence of iodine to form ethyl di-iodostanni-diacetate, $SnI_2(CH_2\cdot CO_2Et)_2$. Compounds of this type differ from the alkyl compounds of the metals in being completely decomposed by water and alkalis, thus:

$$SnI_2(CH_2\cdot CO_2Et)_2 + 2H_2O = 2CH_3\cdot CO_2Et + SnO_2 + 2HI.$$

They appear to yield salts when treated with silver nitrate or sulphate, but so far these have not been separated from their decomposition products. Treated with the Grignard reagent they give the corresponding tin tetra-alkyls.

Ethyl di-iodostanni-diacetate, m. p. 101·5° (corr.), crystallises from carbon tetrachloride on addition of ether in colourless, odourless needles. It is decomposed by baryta into ethyl acetate, stannic oxide, and hydriodic acid. With magnesium phenyl bromide and magnesium ethyl bromide, it gives tin tetraphenyl and tin tetraethyl respectively.

Ethyl di-iodostanni-di-o-benzoate, obtained by heating ethyl *o*-iodo-

benzoate (5 grams), tin foil (1·2 grams), and a little iodine, in a closed tube during five days at 150°, crystallises in greyish-yellow, microscopic needles, and is practically insoluble in all solvents. T. A. H.

$\Delta^{1:3}$-Dihydrobenzene [$\Delta^{1:3}$-*cyclo*Hexadiene]. NICOLAI ZELINSKY and ALEXANDER GORSKY (*Ber.*, 1911, **44**, 2312—2316*).—Doubts have been expressed by Brühl (Abstr., 1908, ii, 1002) and by Harries and von Splawa-Neyman (Abstr., 1909, i, 218) as to the accuracy of the data published by the authors regarding $\Delta^{1:3}$-*cyclo*hexadiene (Abstr., 1908, i, 619, 722), the latter suggesting that the apparent absence of optical exaltation in this hydrocarbon, in spite of the presence of conjugated double linkings, was due to the occurrence of *cyclo*hexene in the material examined. The authors find that when quinoline reacts with 1 : 2-dibromo*cyclo*hexane, the products obtained depend on the relative quantities used and the method of mixing. When the dibromo-derivative is added drop by drop to quinoline in excess, the product is a mixture of *cyclo*hexadiene and *cyclo*hexene, but the material they originally worked with could not have contained more than a trace of *cyclo*hexene. Further, determinations of the molecular refractions of mixtures of $\Delta^{1:3}$-dihydro-*m*-xylene (Klages, Abstr., 1907, i, 597) with 1 : 3-dimethyl*cyclo*hexene (Abstr., 1902, i, 2) show that the latter does not mask the optical exaltation of the former to any considerable extent. Moreover, the ultra-violet absorption spectra of the two *cyclo*hexadienes examined by the authors (*loc. cit.*) are normal and similar, indicating that the hydrocarbon now under discussion is homogeneous.

Bromo-Δ^1-cyclo*hexene*, b. p. 164—166°, or 69°/35 mm., D_4^{20} 1·3901, n_D^{20} 1·5134, obtained as a by-product in the action of quinoline on 1 : 2-dibromo*cyclo*hexane, combines with bromine to form a *dibromide*, b. p. 138—140°/16 mm., and is oxidised by permanganate to adipic acid.

$\Delta^{1:3}$-*cyclo*Hexadiene combines with hydrogen bromide to form a hydrobromide, b. p. 80—85°/39 mm. This combines with bromine to form a *tribromide*, b. p. 150°/15 mm., and is oxidised by permanganate to a dibasic hydroxy-acid, $C_6H_{10}O_5$, m. p. 93—94°, which distils almost unchanged at 240°/20 mm. The formation of this dibasic hydroxy-acid on oxidation renders improbable the constitution assigned to this hydrobromide by Crossley (Trans., 1904, **85**, 1422). T. A. H.

Tetramethyl*cyclo*heptatriene. HANS RUPE and W. KERKOVIUS (*Ber.*, 1911, **44**, 2702—2713).—The action of magnesium methyl iodide on eucarvone yields a tetramethyl*cyclo*heptatriene,

$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CMe{:}CH{\cdot}CMe_2}\\ \mathrm{CH{\cdot}CH{=}CH}\end{matrix} \text{ or } \mathrm{CMe}{<}\begin{matrix}\mathrm{C({:}CH_2){\cdot}CH_2{\cdot}CMe_2}\\ \mathrm{CH{-\!\!-}CH{=\!=}CH}\end{matrix},$$

which is a tetramethyl derivative of the *cyclo*heptatriene prepared by Ladenburg (Abstr., 1883, 670) and Willstätter (Abstr., 1901, i, 223, 649). In one instance the corresponding *tertiary alcohol*, b. p. 96—97°/11 mm., was also obtained, but this could not be obtained pure, as it undergoes partial decomposition on distillation with formation of the tetramethyl*cyclo*heptatriene. Further, a slight variation in the method of preparing the latter results in its admixture with

* and *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1102—1107.

two dimeric, isomeric methyl derivatives of dihydroeucarvone $(C_{11}H_{18}O)_2$.

*Tetramethyl*cyclo*heptatriene*, $C_{11}H_{16}$, is a colourless, mobile oil, b. p. 67—68°/11 mm., D^{20} 0·8687, n_D^{20} 1·50660. The optical exaltation (compare Auwers and Eisenlohr, Abstr., 1910, ii, 365, 367), +0·9, is exactly what is observed for a pair of conjugated ethylene linkings with a side-chain at one of the end carbon atoms; the fact that the three conjugated double linkings of the above formulæ do not give a considerably higher exaltation than 0·9 seems to be a new proof for the assumption made by Auwers and Eisenlohr (*loc. cit.*) that central disturbances (side-chains) may partly or completely annul the optical anomaly of a conjugated linking. It is more stable than methylmenthatriene (compare Rupe and Liechtenhan, Abstr., 1906, i, 374), and yields a *dihydrobromide*, $C_{11}H_{18}Br_2$. When reduced by sodium in amyl alcohol solution, it yields a mixture of di- and tetra-hydro-derivatives, whilst in ethyl alcohol, it gives the pure dihydro-compound, *tetramethyl*cyclo*heptadiene*, $C_{11}H_{18}$, b. p. 64·5—65·5°/12 mm., D^{20} 0·8491, n_D^{20} 1·47643. Which pair of conjugated double linkings is thus easily reduced is not known.

The two methyl derivatives of dihydroeucarvone have the following properties: (*A*) The less readily soluble form gives shining, white, monosymmetric leaflets, m. p. 177—178°. That its *oxime*, $C_{11}H_{19}ON$, decomposing at 265°, and its *semicarbazone*, decomposing at 259°, and also those of compound *B*, are likewise dimeric is indicated by the high melting points. (*B*) This modification forms four-sided, prismatic crystals, m. p. 142—143°; its *oxime* is found to be a mixture of two compounds, m. p.'s 204—205° and 265° respectively, the latter being identical with the oxime of *A*. Unlike eucarvone, the compounds *A* and *B* decolorise permanganate in acetic acid solution only after some minutes; the conclusion is hence drawn that these compounds contain no ethylene linking, and that they are probably stereoisomerides of the structure: $CH_2<\begin{matrix}CO-CHMe-CH\cdot CH-CHMe-CO \\ CMe_2\cdot CHMe\cdot CH\cdot CH\cdot CHMe\cdot CMe_2\end{matrix}>CH_2$.

These results render it highly probable that methylmenthatriene contains two conjugated double linkings. T. H. P.

Δ^3-Butenylbenzene. C. N. Riiber (*Ber.*, 1911, 44, 2391—2393).—Attempts to prepare Δ^3-butenylbenzene, $C_6H_5\cdot CH_2\cdot CH_2\cdot CH:CH_2$, have previously given only Δ^2-butenylbenzene. On condensing allyl bromide and benzyl chloride by means of sodium, it is now shown that, in addition to diallyl and dibenzyl, a hydrocarbon, b. p. 64°/10 mm., is formed. This is proved to be Δ^3-*butenylbenzene*, since it yields phenylpropionic acid when oxidised by permanganate in acetone.

The hydrocarbon is a mobile, strongly refractive and dispersive liquid, with an odour similar to that of cress leaves; it has D_4^{20} 0·8831, n_D^{20} 1·5059. E. F. A.

Preparation of 2:4:6-Trinitrobenzene from Halogenated Trinitrobenzenes. Jacob. Meyer (D.R.-P. 234726).—When 1-chloro-2:4:6-trinitrobenzene is vigorously boiled during two hours with finely divided copper in a neutral solvent (such as alcohol), the

chlorine is eliminated and pure 2 : 4 : 6-trinitrobenzene separates from the cooled solution. The metals capable of reacting in this manner are copper, zinc, magnesium, brass, iron, or aluminium, whilst methyl, ethyl, or amyl alcohols, benzene, acetone, or ether can be employed as solvent. F. M. G. M.

Barium Oxide as a Reducing Agent. Reduction of Nitrobenzene to Nitroso- and Azo-benzene, Aniline, Phenazine, and Ammonia. TH. ZEREWITINOFF and IWAN VON OSTROMISSLENSKY (*Ber.*, 1911, **44**, 2402—2409).—When nitrobenzene vapour is passed over a layer of barium oxide heated in a tube at 230°, nitrosobenzene is at first formed, but the reduction goes further, and, in addition to the chief product, azobenzene, considerable quantities of phenazine and aniline and traces of ammonia are formed. Nitrobenzene is unchanged when passed over heated coal or pumice, and also when calcium or strontium oxide is substituted for barium oxide.

p-Nitrotoluene under similar conditions gives *p*-toluidine and a crystalline, yellowish-red azotoluene, m. p. 139°. *o*-Nitrotoluene gives exclusively *o*-toluidine. *m*-Dinitrobenzene is not altered by barium oxide.

With barium hydroxide and nitrobenzene only aniline and phenazine are formed.

The formation of nitroso- and azo-benzene is due to the tendency of barium to form peroxide.

The following new double compounds of phenazine are described: *phenazine-quinol*, $C_6H_4(OH)_2,2C_{12}H_8N_2$, forms orange-yellow needles, m. p. 232° (decomp.); *phenazine-resorcinol*, $C_6H_4(OH)_2,2C_{12}H_8N_2$, forms bright yellow needles, m. p. 213·5°; *phenazine-catechol* crystallises in stellate aggregates of bright yellow needles m. p. 184°. E. F. A.

Quantitative Investigation of the Sulphonation of Toluene. ARNOLD F. HOLLEMAN and P. CALAND [with T. VAN DER LINDEN and J. P. WIBAUT] (*Ber.*, 1911, **44**, 2504—2522).—The quantities of *o*-, *m*-, and *p*-toluenemonosulphonic acids formed by the action of sulphuric acid on toluene under various conditions have been investigated. The method consisted in sulphonation of the toluene and transformation of the mixture of sulphonic acids into the corresponding sulphonyl chlorides. The composition of the latter mixture was deduced from its first and second melting points.

The influence of temperature, concentration of acid, and amount of acid was investigated. Increase of temperature favoured the production of para- and meta-acid at the expense of ortho-acid. Concentration of acid, between the limits of 96% and 100%, appeared to be without influence. Increase in the amount of acid favoured the production of ortho-acid at low temperatures, but this influence was masked at higher temperatures by the effect due to rise of the latter.

The presence of *m*-toluenesulphonic acid among the products of the sulphonation of toluene has been definitely proved by the isolation of *m*-toluenesulphonamide (m. p. 107°).

The addition of potassium sulphate, mercurous sulphate, and

silver sulphate has been shown to have no influence on the course of sulphonation.

The action of chlorosulphonic acid on toluene has also been studied. *p*-Toluenesulphonic acid is again the main product.

The possible interconversion of the isomeric toluene monosulphonic acids has been investigated. *m*-Toluenesulphonic acid was found unaltered after being heated with sulphuric acid during six hours at 100°. At 35° and at 75°, the transformation of ortho- and para-acids into one another occurs very slowly. At 100° this action has a certain influence on the relative proportion of acids formed during sulphonation. H. W.

Preparation of Chloroalkylarylsulphonyl Chlorides. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 234913).—When derivatives of *p*-toluenesulphonyl chloride are treated with phosphorus pentachloride and chlorine introduced at a temperature of 120—140°, chlorination takes place in the side-chain, yielding the corresponding chlorobenzyl derivatives.

ω-Chlorotoluene-p-*sulphonyl chloride*, $C_7H_6O_2Cl_2S$, colourless needles, m. p. 64—65°, b. p. 183—185°/15 mm., was obtained from *p*-toluenesulphonyl chloride; and *m*-toluenesulphonyl chloride furnished *ω-chlorotoluene*-m-*sulphonyl chloride*, colourless crystals, m. p. 65°, b. p. about 190°/21 mm.

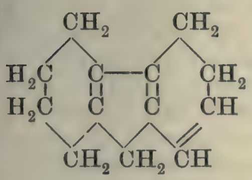
ω-2-*Dichlorotoluene*-p-*sulphonyl chloride*, a colourless oil, b. p. 185—190°/15·5 mm., was obtained from *o*-chlorotoluene-*p*-sulphonyl chloride, whilst 6-chlorotoluene-3-sulphonyl chloride furnished ω-6-*dichlorotoluene*-3-*sulphonyl chloride*, colourless crystals, b. p. 182—186°/14 mm. F. M. G. M.

Preparation of a Mixture of 1:4- and 1:5-Dichloronaphthalenes. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 234912).—The preparation of dichloronaphthalenes has not in the past been technically satisfactory; it is now found that by working at low temperatures and in the presence of a halogen carrier that a mixture containing over 80% of 1 : 4- and 1 : 5-dichloronaphthalenes is obtained, the remainder consisting of the 1 : 2- and 1 : 7-isomerides. The naphthalene, accompanied by some freshly sublimed ferric chloride, is treated in carbon tetrachloride solution with chlorine at – 10° to 0°; on fractional distillation the greater part distils at 170—190°/40 mm., and when crystallised from alcohol furnishes a colourless, crystalline powder (m. p. 50—60°) consisting of the 1 : 4- and 1 : 5-dichloronaphthalenes.

An alternative separation is to treat the crude mixture with sulphuric acid at the ordinary temperature during twenty hours, when the 1 : 4- and 1 : 5-derivatives remain unchanged, whereas the isomerides are converted into soluble sulphonic acids. F. M. G. M.

A Constituent of Coal. AMÉ PICTET and LOUIS RAMSEYER (*Ber.*, 1911, **44**, 2486—2497).—A French gas coal from Montrambert was extracted with boiling benzene and also submitted to distillation under diminished pressure. The extract and distillate were fractionated and shown to contain hexahydrofluorene. On fractionating the extract it was found impossible to obtain fractions of constant

boiling point, since the lower boiling fractions readily polymerise. In all fractions, analysis showed the ratio C : H to be the same. For investigation, a fraction was used having a b. p. 110—120°/10 mm., 240—250°/ordinary pressure, and D^{20} 0·920. This, when passed through a red-hot tube, yielded fluorene, m. p. 112—113°. When treated with bromine in carbon disulphide solution, dibromofluorene, m. p. 166—167°, was formed, whilst when placed in a desiccator with bromine, it became converted into monobromofluorene, m. p. 101—102°.



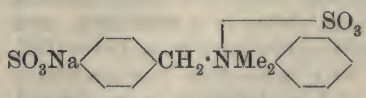
On oxidation with potassium permanganate, acetic, adipic, and oxalic acids were formed. Nitration yielded a mixture of products from which, on reduction and benzoylation, a dibenzoyldiaminotetrahydrofluorenol, m. p. 150°, was obtained. From the above experiments the annexed formula is proposed for hexahydrofluorene. When distilled under diminished pressure at a temperature not exceeding 450°, the same coal yielded a series of more complex fractions in which the ratio C : H was not constant. H. W.

Triphenylmethyl Peroxide. The Chemistry of Free Radicles. HEINRICH WIELAND (*Ber.*, 1911, **44**, 2550—2556).—Elaborating his conception, already applied to $\cdot NPh_2$ and $\cdot CPh_3$ (this vol., i, 569), that a free radicle R, containing hydrogen, reacts by intermolecular autoreduction and autoxidation in accordance with the scheme $4(R^{-H})H \longrightarrow 2RH + (R^{-H})_2$, the author suggests that peroxides may dissociate thus: $R\cdot O\cdot O\cdot R \longrightarrow 2R\cdot O\cdot$; the resulting radicle may or may not react further, as in the preceding scheme; thus the spontaneous decomposition of triphenylmethyl peroxide in boiling xylene is assumed to result in the formation of the radicle $CPh_3\cdot O\cdot$. A small portion of this is converted into triphenylcarbinol, but the bulk of it, 60—70%, undergoes rearrangement to phenoxydiphenylmethyl, $OPh\cdot CPh_2\cdot$, by the polymerisation of which diphenylbenzpinacone, the chief product of the decomposition of the peroxide, is formed. *Benzpinaconediphenyl ether*, $OPh\cdot CPh_2\cdot CPh_2\cdot OPh$, forms colourless plates, and has m. p. about 196°, darkening at 135°, by the usual process, but when heated in carbon dioxide, it becomes yellow at 150° and melts at 215° to a garnet-red liquid. When reduced by zinc and boiling acetic acid, it is converted into phenol and benzhydryl acetate, together with a little *substance*, m. p. 198°, which probably has the constitution $OPh\cdot CPh_2\cdot C_6H_4\cdot CHPh\cdot OPh$.

When heated at 230—240° in the absence of air, benzpinaconediphenyl ether undergoes the reverse change to phenoxydiphenylmethyl, which, in accordance with the preceding scheme (except that the phenoxy-group wanders instead of a hydrogen atom), is converted into tetraphenylethylene and *diphenoxydiphenylmethane*, $CPh_2(OPh)_2$, m. p. 132°; the latter is readily hydrolysed to phenol and benzophenone by boiling acetic and concentrated hydrobromic acids. Since a little phenol and benzophenone are obtained by the depolymerisation of benzpinaconediphenyl ether by heat, especially in boiling xylene, it is probable that a portion of the phenoxydiphenylmethyl suffers the

normal autoreduction and autoxidation, yielding substances from which the phenol and benzophenone are produced. C. S.

Preparation of Phenylbenzyldimethylammoniumdisulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 234915 and 234916).—*Sodium phenylbenzyldimethylammoniumdisulphonate* (annexed formula), a yellow, hygroscopic powder, is prepared by heating sodium benzylmethylanilinedisulphonate with methyl sulphate at 50°, and subsequently evaporating under reduced pressure; when heated with aqueous ethylaniline, it furnishes benzylethylanilinesulphonic acid and dimethylaniline-3-sulphonic acid (dimethylmetanilic acid). The second patent states that the methyl sulphate can be replaced by methyl *p*-toluenesulphonate (or other methyl esters), in which case calcium benzylmethylanilinedisulphonate in the presence of calcium carbonate (or hydroxide) is employed, and the mixture heated at 60°; after separation of the toluenesulphonic acid by known methods, *calcium phenylbenzyldimethylammoniumdisulphonate* is obtained as a yellow powder, which is readily soluble in water. F. M. G. M.



Kinetics of Ammonium Salts. HANS VON HALBAN (*Zeitsch. physikal. Chem.*, 1911, **77**, 719—734).—Polemical against Wedekind and Paschke (compare Abstr., 1909, ii, 722; Wedekind and Paschke, Abstr., 1908, i, 723; this vol., i, 628). The contention of these investigators that the rate of decomposition of dissolved quaternary ammonium salts is related to the dissociating power of the solvent is not valid. As already pointed out (*loc. cit.*), the reactions are relatively slow in solvents containing hydroxyl groups. The influence of the corresponding nitrate on the rate of decomposition of *d*-phenylbenzylmethylpropylammonium iodide is much smaller than Wedekind and Paschke state, and an alternative explanation of this effect is given. The very small temperature-coefficient (1·02 for a rise of temperature of 10°) given by these authors for the rate of formation of a quaternary ammonium salt is due to experimental error; the true value is 1·7.

Phenylbenzyldiethylammonium iodide forms a crystalline compound with chloroform, and *p*-bromophenylbenzyldimethylammonium iodide a similar compound with bromoform, which contains a molecule of the solvent. In contrast to solutions in chloroform, quaternary ammonium salts are only slightly polymerised in tetrachloroethane. G. S.

The Metallic Salts of Trinitrophenols and Trinitrocresols. HERMANN KAST (*Zeitsch. ges Schiess-sprengstoffwesen*, 1911, **6**, 7—9, 31—34, 67—70. Compare *Annalen*, 1843, **48**, 336; *Zeitsch. Chem.*, 1865, 189).—A description of the preparation of the following compounds in crystalline form, with special details as to their explosive qualities.

Salts of picric acid.—Potassium, ammonium, and sodium: reddish-yellow needles, the latter containing one molecule of water of crystallisation.

Calcium, $(C_6H_2O_7N_3)_2Ca,3H_2O$ (also 5 or $10H_2O$); barium, $(C_6H_2O_7N_3)_2Ba,3$ or $5H_2O$; magnesium, $(C_6H_2O_7N_3)_2Mg,3H_2O$ (also 5 or $8H_2O$), two mols. of which persist until 130°, and zinc, $(C_6H_2O_7N_3)_2Zn,8H_2O$ (also 2, 6 or $9H_2O$), two mols. of which persist until 130°, all form reddish-yellow needles. Ferrous,

$$(C_6H_2O_7N_3)_2Fe,7 \text{ or } 8H_2O,$$

transparent, green leaflets. *Ferric*, $(C_6H_2O_7N_3)_3Fe,11H_2O$, reddish-yellow crystals. *Cuprous*, $(C_6H_2O_7N_3)_2Cu,5H_2O$ (also 4 or $11H_2O$), two mols. of which persist until 130°, forms small, greenish-yellow needles. *Silver*, reddish-yellow, glistening needles unstable in light. *Aluminium*, $(C_6H_2O_7N_3)_2Al(OH),7H_2O$, small, reddish-yellow needles. *Lead*, $(C_6H_2O_7N_3)_2Pb,1$ or $4H_2O$, a yellow, crystalline powder.

Salts of trinitrocresol.—Potassium, $C_7H_4O_7N_3K$. *Sodium*,

$$C_7H_4O_7N_3Na,2H_2O,$$

small, yellow needles. *Ammonium* and *calcium*, $(C_7H_4O_7N_3)_2Ca,4H_2O$, reddish-yellow needles. *Barium*, $(C_7H_4O_7N_3)_2Ba,H_2O$, small, sulphur-yellow leaflets. *Magnesium* and *zinc*, reddish-yellow powders, with $6H_2O$, three of which in the zinc salt persist until 130°. *Cuprous*, $(C_7H_4O_7N_3)_2Cu,2H_2O$, small, greenish-yellow needles, is stable until 130°. Silver, reddish-yellow needles (compare Abstr., 1885, 531). *Aluminium*, $(C_7H_4O_7N_3)_2Al(OH),5H_2O$, reddish-yellow needles, darkening in sunlight. *Lead*, $(C_7H_4O_7N_3)_2Pb,H_2O$, sulphur-yellow leaflets. *Ferrous*, $(C_7H_4O_7N_3)_2Fe,2H_2O$, glistening, greenish-yellow needles, and *ferric*, brown crystals, decomposed by boiling water. F. M. G. M.

Preparation of 4-Chloro-6-nitro-2-aminophenol. Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 234742).—When 4-chloro-2-acetylaminophenol is treated with dilute nitric acid, 4-*chloro-*6-*nitro-*2-*acetylaminophenol*, m. p. 150—160°, is produced, which when hydrolysed by alkali hydroxides yields 4-chloro-6-nitro-2-aminophenol as a yellowish-brown powder. F. M. G. M.

Derivatives of 1 : 2-Dimethylbenzene [*o*-Xylene]. II. Emil Diepolder (*Ber.*, 1911, 44, 2498—2503. Compare Abstr., 1909, i, 786).—The phenylhydrazone of the *o*-4 : 5-xyloquinone described previously, when treated with sodium hyposulphite in alcoholic solution, yields 5-amino-*o*-4-xylenol; the *acetyl* derivative crystallises in thin plates, which sinter at 184°, m. p. 190·5—191°, and when heated gives 5-*vinylideneamino*-o-4-*xylenol*, white needles, m. p. 93—94°.

5-*Acetylamino*-o-4-*xylenyl acetate* forms fine, white, silky needles, m. p. 156—157°, and 5-*diacetylamino*-o-4-*xylenyl acetate* crystallises in hexagonal plates, m. p. 100·5—101·5°.

o-Aminophenol when treated with acetic anhydride and sodium acetate yields o-*diacetylaminophenyl acetate* in long, colourless needles, m. p. 78—79°.

4 : 5-*Dihydroxy*-m-*xylene*, obtained by the reduction of *o*-4 : 5-xyloquinone with aqueous sulphurous acid or sodium hyposulphite, forms colourless, slender prisms sintering at 85°, m. p. 87—88°.

Attempts to prepare a colourless modification of *o*-4 : 5-xyloquinone were fruitless. H. W.

Chloroguaiacols. TEMISTOCLE JONA and G. B. POZZI (*Gazzetta*, 1911, **41**, i, 722—737).—5-*Aminoguaiacol hydrochloride*, $C_7H_{10}O_2NCl$, from 5-nitro-1-acetylguaiacol (compare Cousin, Abstr., 1899, i, 200) forms pale greenish-white crystals. 5-*Aminoguaiacol*, $C_7H_9O_2N$, was obtained in grey crystals, m. p. 125—127°, which were not quite pure; it gives a reddish-brown coloration with ferric chloride. 5-*Benzoylaminoguaiacol benzoate*, $C_{21}H_{17}O_4N$, forms colourless crystals, m. p. 162—164°, and does not give a coloration with ferric chloride. 5-*Acetylaminoguaiacol*, $C_9H_{11}O_3N$, forms colourless crystals, m. p. 116—119°, and gives the phenol reaction with ferric chloride. 5-*Chloroguaiacol*, $C_7H_7O_2Cl$, obtained by the Sandmeyer reaction from aminoguaiacol, has b. p. 237—239°/760 mm. (corr.), m. p. 161—163·5°. It gives a yellow coloration with ferric chloride. 5-*Chloroguaiacol benzoate*, $C_{14}H_{11}O_3Cl$, crystallises in long, colourless needles, m. p. 56—58°. 5-*Chloroguaiacol acetate*, $C_9H_9O_3Cl$, crystallises in colourless leaflets, m. p. 42—44°. 5-*Chloroguaiacolethyl ether*, $C_9H_{11}O_2Cl$ (prepared with ethyl iodide), forms colourless crystals, m. p. 49—51°.

4-Aminoguaiacol acetate is obtained by reducing with phenylhydrazine the acetyl derivative of benzeneazoguaiacol.

4-*Acetylaminoguaiacol*, $C_9H_{11}O_3N$ (from 4-aminoguaiacol), forms colourless crystals, m. p. 111—113°, and gives the phenol reaction with ferric chloride. 4-*Chloroguaiacol*, $C_7H_7O_2Cl$ (prepared by the Sandmeyer reaction from 4-aminoguaiacol acetate), is a colourless, crystalline substance, m. p. 158—161°, b. p. 241—243°/760 mm. (corr.). Its *benzoyl* derivative, $C_{14}H_{11}O_3Cl$, crystallises in colourless scales having a mother-of-pearl lustre, m. p. 79—80°.

The benzoyl derivative of chloroguaiacol obtained by Peratoner and Ortoleva (Abstr., 1898, i, 641) had m. p. 76—77°, and was probably identical with the derivative just described. R. V. S.

Preparation of 1:4-Dihydroxynaphthalene Monoalkyl Ethers. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P 234411).—A satisfactory yield of 1:4-dihydroxynaphthalene monoalkyl ethers can be obtained by heating 4-amino-α-naphthol hydrochloride with alcohol during twelve hours at 170—180°. When methyl alcohol is employed under these conditions, 200 parts of the aminonaphthol yield 120—130 parts of the *monomethyl ether*, reddish-white crystals, m. p. 131°. F. M. G. M.

Some Derivatives of Hydroxyquinol. IV. GUIDO BARGELLINI and ERMANNO MARTEGIANI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 18—25. Compare this vol., i, 68, 305).—In the course of attempts to demonstrate the structure of 2:4:5-trimethoxypropiophenone and of its dimethyl ether, previously described, the authors have prepared some new derivatives of these substances. Trimethoxypropiophenone is not acted on by bromine and sodium hydroxide (compare Störmer and Wehln, Abstr., 1903, i, 40).

Hydroxyquinol trimethyl ether may be prepared with good yield by the action of methyl sulphate on triacetylhydroxyquinol, a concentrated solution of sodium hydroxide being added in small portions. Hexamethoxydiphenyl is not formed when the reaction is carried out in this way.

The 2-hydroxy-4 : 5-dimethoxypropiophenone previously mentioned crystallises in small, colourless needles, m. p. 124—126° (softening at 120°). The *acetyl* derivative, $C_{13}H_{16}O_5$, also crystallises in needles, m. p. 117—118°. The *benzoyl* derivative, $C_{18}H_{18}O_5$, forms long needles, m. p. 110—111°

2 : 4 : 5-*Trimethoxypropiophenonephenylhydrazone* has m. p. 113°. 2 : 4 : 5-*Trimethoxypropiophenonemonoxime* (prepared with amyl nitrite), $C_{12}H_{15}O_5N$, crystallises in scales having a slight yellowish-green colour, and has m. p. 146—148°. It gives a deep reddish-brown coloration with an alcoholic solution of nickel acetate. When it is treated with hydroxylamine hydrochloride the *dioxime*, $C_{12}H_{16}O_5N_2$, is formed, which crystallises in prismatic needles, m. p. 206—207°. An alcoholic solution of the substance yields with an alcoholic solution of nickel acetate a bright red precipitate; with ammonium palladichloride it gives a pale yellow substance; with ferrous sulphate in the presence of pyridine an intense red coloration and a red precipitate are produced. The substance seems, therefore, to be a *syn*dioxime (compare Tschugaeff, Abstr., 1908, i, 554). When the above monoxime is treated with phenylhydrazine, the *oxime-phenylhydrazone*, $C_{18}H_{21}O_4N_3$, is obtained as a white, crystalline powder, m. p. 246—248°. By boiling the monoxime, dioxime, or oxime-phenylhydrazone with dilute acids, small quantities of a crystalline *substance*, m. p. 133°, are obtained.

R. V. S.

Some Derivatives of Hydroxyquinol. V. GUIDO BARGELLINI and S. AURELI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 118—124. Compare this vol., i, 305).—Hydroxy-ketones related to hydroxyquinol have been prepared by the action of persulphates on less highly oxygenated phenols in alkaline solution (compare Kumagai and Wolffenstein, Abstr., 1908, i, 159). It is further found that the saponification of 2 : 4 : 5-trimethoxyacetophenone by means of hydrobromic acid (compare Stoermer, Abstr., 1908, i, 190) yields 2 : 4-dihydroxy-5-methoxyacetophenone.

The action of potassium persulphate or of ammonium persulphate on 2-hydroxy-4-methoxyacetophenone (paeonol) in alkaline solution under diverse conditions yields 2 : 5-*dihydroxy*-4-*methoxyacetophenone*, $C_9H_{10}O_4$, which crystallises in white scales having a yellow tinge, m. p. 164°. When dissolved in concentrated sulphuric acid, it gives a yellowish-green coloration. Its aqueous solution gives with ferric chloride a red coloration. The *acetyl* derivative, $C_{13}H_{14}O_6$, forms small, colourless needles, m. p. 118—119°. The *benzoyl* derivative is a yellowish-white, crystalline powder, m. p. 215°. When sodium peroxide is used instead of a persulphate in the above oxidation, the paeonol remains unchanged, whilst when hydrogen peroxide is employed a mixture of products is obtained. Esterification of 2 : 5-dihydroxy-4-methoxyacetophenone with methyl sulphate yields both the trimethoxy- and dimethoxy- derivatives. The former can be extracted with ether from the alkaline solution, and is identical with the 2 : 4 : 5-trimethoxyacetophenone, m. p. 101—102°, previously described (Bargellini and Avrutin, this vol., i, 68). From the alkaline liquid after acidification, 2-*hydroxy*-4 : 5-*dimethoxyacetophenone*, $C_{10}H_{12}O_4$,

can be extracted with ether; it crystallises in yellowish-white needles, m. p. 114—115°. Its aqueous solution gives a green coloration with ferric chloride. The *acetyl* derivative, $C_{12}H_{14}O_5$, forms small, colourless needles, m. p. 146—147°. With anisaldehyde, 2-hydroxy-4 : 5-dimethoxyacetophenone yields *2′-hydroxy* 4 : 4′ : 5′-*trimethoxychalkone*, which crystallises in small, red needles, m. p. 130°. It dissolves in concentrated sulphuric acid, giving an intense orange-yellow coloration.

When trimethoxyacetophenone in acetic acid solution is boiled for two hours with hydrobromic acid (D 1·47), 2 : 4-*dihydroxy*-5-*methoxyacetophenone*, $C_9H_{10}O_4$, is produced; it forms yellowish-white needles, m. p. 166°. Its aqueous solution gives a red coloration with ferric chloride. The *acetyl* derivative, $C_{13}H_{14}O_6$, crystallises in long, colourless needles, m. p. 127—128°. R. V. S.

A Nitroso-compound of Dimethoxyphenol, and its Derivatives. RUDOLF FABINYI and TIBOR SZÉKI (*Ber.*, 1911, **44**, 2293—2298).—The substance obtained by boiling asaronic acid in aqueous solution with sodium nitrite, and formerly supposed to be 4 : 5-dimethoxy-*o*-benzoquinoneoxime or its tautomeride (Abstr., 1907, i, 45), is now shown to be 2 : 5-dimethoxy-1 : 4-benzoquinoneoxime or the tautomeric 4-nitroso-2 : 5-dimethoxyphenol, and a number of its derivatives are described. The substance on repeated crystallisation from hot acetic acid forms transparent, lustrous citron-yellow needles identical in composition with the red form described previously.

On methylation with methyl sulphate, it gives 4-*nitroso*-1 : 2 : 5-*trimethoxybenzene*, m. p. 191°, which crystallises in long, reddish-yellow needles from alcohol. The reduction to 4-amino-2 : 5-dimethoxyphenol, m. p. 157° (*loc. cit.*), is best effected by ammonia and hydrogen sulphide; the *acetylamino*-compound, m. p. 180°, crystallises from boiling water, and the *diacetyl* derivative, m. p. 190°, from either water or boiling alcohol; the *dipropionyl* derivative, m. p. 131°, also crystallises from alcohol. On oxidation with 50% nitric acid the aminodimethoxyphenol yields 2 : 5-dimethoxy-1 : 4-benzoquinone (compare Schüler, Abstr., 1907, i, 700), and on treatment with ethyl chlorocarbonate in alcohol gives *ethyl* 4-*hydroxy*-2 : 5-*dimethoxyphenylaminoformate*, m. p. 143°, which crystallises from benzene in glancing leaflets, and is readily soluble in alcohol, chloroform, or acetic acid; the *acetyl* derivative of this, m. p. 135°, crystallises from hot alcohol, and the *carboxymethyl ether*, $CO_2H·CH_2·O·C_6H_2(OMe)_2·NH·CO_2Et$, m. p. 108°, obtained by condensation with ethyl bromoacetate in presence of sodium and alcohol, crystallises from alcohol.

4-*Acetylamino*-2 : 5-*dimethoxyphenoxyacetic acid*,

$$NHAc·C_6H_2(OMe)_2·O·CH_2·CO_2H,$$

m. p. 172°, obtained by condensing ethyl bromoacetate with 4-hydroxy-2 : 5-dimethoxyacetanilide, forms colourless crystals from alcohol.

Several of the substances described exert an antipyretic action, which is, however, less marked than that due to phenacetin.

T. A. H.

Aromatic Tellurinium Compounds with the same Hydrocarbon Residue. CHARLES LEDERER (*Ber.*, 1911, 44, 2287—2292).—Tellurium tetrachloride reacts with the Grignard reagent to form telluronium compounds containing three aromatic hydrocarbon residues. These react in part with the Grignard reagent present to form the corresponding diaryl tellurides and diaryl hydrocarbons, thus: $R_3TeCl + R{\cdot}MgBr = R_2Te + R_2 + MgClBr$. In addition, the diaryltelluride so formed reacts with hydrochloric acid subsequently added, in presence of air, to form some diaryltellurinium dichloride, which in turn is decomposed on addition of water, forming a basic chloride, thus:

$$TeR_2 + 2HCl + O = TeR_2Cl_2 + H_2O = TeR_2Cl{\cdot}OH + HCl.$$

In these equations R represents an aromatic hydrocarbon residue. In certain cases irregularities were observed. With magnesium *o*-tolyl iodide, no di-*o*-tolyl was formed, but, instead, an unidentified high-boiling hydrocarbon. With magnesium *p*-tolyl bromide, the di-*p*-tolyl obtained was not identical with that of Weiler (Abstr., 1899, i, 490). A description is given of the method used for the separation of all the substances formed.

Triphenyltellurinium iodide, $TePh_3I$, sinters at 245°, has m. p. 247—249°, and crystallises from hot water in small needles. The corresponding *bromide*, m. p. 259—260°, separates from hot water in small prisms. The *chloride*, m. p. 244—245°, crystallises from dry alcohol on addition of ether in long, slender needles.

*Tri-*p*-tolyltellurinium iodide*, m. p. 232—233° (decomp.), crystallises from alcohol in six-sided tablets. The *bromide*, m. p. 265—266° (decomp.), crystallises from water or from alcohol on addition of ether. The *chloride*, m. p. 260—261°, crystallises in small prisms from dry alcohol on addition of ether.

*Tri-*o*-tolyltellurinium iodide*, m. p. 195—196°, forms small, four-sided columns from water or alcohol on addition of ether. Its aqueous solution is precipitated by picric acid. T. A. H.

Preparation of ω-*p*-Alkylhydroxyphenylethylamines and their *N*-Alkyl Derivatives. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 234795).—It is found that ω-*p*-alkylhydroxyphenylethylamines can be readily prepared by treating primary *p*-alkylhydroxyphenylethyl alcohols with phosphorus pentahalides and subsequently heating the ω-*p*-alkylhydroxyphenylethyl halide so obtained with ammonium hydroxide (or the required alkylamine) in a closed vessel at 100°.

p-*Methoxyphenylethyl alcohol*, m. p. 22°, b. p. 143°/13 mm. (prepared from ethylene chloride and magnesium *p*-anisyl bromide), furnished under these conditions a 50—60% yield of ω-*p*-methoxyphenylethylamine, and when dimethylamine was employed, an 80% yield of ω-*p*-methoxyphenylethyldimethylamine; the intermediate *chloride* has b. p. 100—105°/7 mm.

p-*Ethoxyphenylethyl alcohol*, prepared from ethylene chlorohydrin and magnesium *p*-phenetyl bromide, can also be employed in the foregoing reaction; it has m. p. 40° and b. p. 135—140°/7 mm.; the intermediate *chloride* has b. p. 125—130°/7 mm. F. M. G. M.

Phytosterols of Soy Bean. HERMANN MATTHES and A. DAHLE (*Arch. Pharm.*, 1911, **249**, 436—444. Compare this vol., i, 831; Klobb and Block, Abstr., 1907, i, 521; Keimatsu, this vol., i, 766).—Soy bean oil contains 0·7% of unsaponifiable matter, of which 55% is solid and crystalline, and is composed of stigmasterol 2·4%, and a new phytosterol 97%, and 45% is liquid.

The crude unsaponifiable matter was mixed with light petroleum and the mixture strongly cooled, when it separated into (1) a solid, crystalline product; (2) a solution in light petroleum of a viscous, brown material. The solid product was acetylated and the acetylated product brominated in ether solution, when stigmasterol acetate tetrabromide, m. p. 205—206° (compare Windaus and Hauth, Abstr., 1907, i, 129), separated. The portion of the brominated product soluble in ether was recovered in crystalline form by gradual addition of water to its solutions in alcohol. It proved to be *phytosterol acetate dibromide*, $C_{29}H_{46(or\ 48)}O_2Br_2$, m. p. 125°, and on reduction and subsequent hydrolysis gave the corresponding *phytosterol*, $C_{27}H_{44(or\ 46)}O,H_2O$, m. p. 139°, $[\alpha]_D^{15}$ $-22·83°$.

The liquid product had iodine number 124·4, n_D^{50} $-1·4835$, $[\alpha]_D$ 0°, and gave the colour reactions of the phytosterols. On treatment with digitonin (compare Windaus, Abstr., 1909, i, 172) a small amount of the material separated as a *crystalline additive product*, $[\alpha]_D^{15}$ $-44·66°$ in methyl alcohol, but no separation of the liquid into its components was thereby effected. The liquid has the same empirical composition as the phytosterol referred to above. T. A. H.

Action of Chlorine on "Saccharin." PASQUALE BERTOLO (*Gazzetta*, 1911, **41**, i, 698—705).—When "saccharin" is subjected to the prolonged action of nascent chlorine (from hydrochloric acid and potassium chlorate), *o*-chlorobenzoic acid is obtained. When the duration of the action is more limited, however, a substance is obtained to which the constitution of *potassium* o-*iminosulphobenzoic acid*, $NH\colon SO(OK)\cdot C_6H_4\cdot CO_2H$, is ascribed. In this case "saccharin" is boiled with dilute hydrochloric acid, and potassium chlorate is added from time to time until the "saccharin" is completely dissolved, and the boiling is then continued for a few minutes to expel excess of chlorine. The above-mentioned substance, $C_7H_6O_4NSK$, crystallises from the solution, after concentration, in the form of transparent, colourless, tabular, rhombic crystals [S. Di Franco: $a:b:c = 1·46335:1:1·79093$], m. p. 285—286°. The *barium* salt,

$$C_6H_4<\begin{matrix}CO_2\text{———————}\\SO(\colon NH)\cdot O\end{matrix}>Ba,$$

crystallises with $1\frac{1}{2}HO$, which it loses at 110°. From it the free *acid* may be obtained. When the potassium salt is boiled with 50% potassium hydroxide, ammonia is evolved, and *potassium* o-*sulphobenzoate* is obtained. *Barium sulphobenzoate*, $C_7H_4O_5SBa,2H_2O$, was also prepared. R. V. S.

Preparation of Esters of Cinnamic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 235357).—*Ethylene cinnamate*, a colourless, odourless oil, b. p. 190—195°/11 mm., is prepared by

heating together equal quantities of ethylene glycol and cinnamic acid during thirty hours at 140° in the presence of concentrated sulphuric acid. *Glycerol monocinnamate*, a yellow, oily liquid, and *ethylene chlorohydrin ethoxycinnamate*, a yellow liquid, and other substances allied to the constituents of Peru balsam are discussed in the original. F. M. G. M.

Refraction of Light by *allo-* and *iso-*Cinnamic Acids. Hans Stobbe and Fritz Reuss (*Ber.*, 1911, **44**, 2735—2739).—Two specimens of *allo*cinnamic acid were examined: (1) m. p. 68°, prepared by the action of hydrogen on phenylpropiolic acid in presence of colloidal palladium, and (2) m. p. 67—68°, prepared from an aniline salt.

With acid (1) the following refractometric measurements were made on the melted acids: (*a*) of *allo*cinnamic acid from 71·7° to 52·0°; (*b*) of *iso*cinnamic acid, m. p. 58°, from 70·7° to 55·8°, and (*c*) of *iso*cinnamic acid, m. p. 42°, from 45·8° to 51·1°. The results, plotted against the temperature, all fell on a straight line, so that the refraction of all three acids is continuous and diminishes proportionally with the temperature, as happens with compounds known to be chemical individuals. The results obtained with *allo*cinnamic acid (2) from 77·3° to 22·6° also fell on a straight line with the same slope as, and only very slightly distant from, that of the (1) acids. Fused *allo-* and *iso-*cinnamic acids are hence to be regarded as optically identical. T. H. P.

Transformations of *allo-* and *iso-*Cinnamic Acids in the Fused and Crystalline States. Hans Stobbe (*Ber.*, 1911, **44**, 2739—2754. Compare preceding abstract).—The author has confirmed and extended the observations of Liebermann (Abstr., 1903, i, 255; 1909, i, 303; 1910, i, 36, 175), Biilmann (Abstr., 1909, i, 155, 382; 1910, i, 346), Erlenmeyer (Abstr., 1891, 200; 1896, i, 46), Erlenmeyer, jun. (Abstr., 1906, i, 429; 1907, i, 318; 1909, i, 156, 647, 648), Paal and Hartmann (Abstr., 1909, i, 926), and Stoermer (Abstr., 1910, i, 114) on *allo-* and the two *iso-*cinnamic acids. In the experiments described, extreme care was taken to avoid accidental seeding of the fused or crystalline masses under examination.

By crystal-seeding, the crystalline acid m. p. 42° can be converted into that with m. p. 68° (with development of considerable heat) or 58°, and the latter into that with m. p. 68°.

When the crystalline 42°-acid is heated in a sealed tube for eighty hours at 37°, or the 58°-acid for thirty hours at 52°, no change occurs; but the 42°-acid is transformed completely into the 68°-acid in five minutes at −80° and almost instantaneously at −180°; with the 58°-acid similar conversion takes place in three hours at −80° and in ten minutes at −180°. The 68°-acid undergoes no change at either −80° or −180°, so that, in all cases, the most labile acid (42°) is converted, by grinding (Liebermann, *loc. cit.*) or cooling, into the stable *allo*-acid more rapidly than is the less labile form (58°). The two labile acids appear to be only metastable forms of a single chemical compound, trimorphous *cis*-cinnamic acid.

If a few milligrams of the fused 68°-acid, heated for 0·5—5 minutes to 72—80°, are cooled to the ordinary temperature or to −14°, the result was almost always the 42°-acid, but occasionally the 68°-acid; but 0·05—1·0 gram of the 68°-acid, on heating to 80—105° for ten minutes or for several hours, and then cooling to the ordinary temperature or to −14°, solidifies to the 68°-acid more frequently than to the 42°-acid.

The observation of Liebermann and of Biilmann, that the fused 42°- and 58°-acids always solidify to the 42°-acid on cooling to the ordinary temperature or to 0°, is confirmed, but if the cooling is effected in a mixture of ice and salt, sometimes the 42°-acid and sometimes the 58°-acid separates; separation of the former can always be recognised by the slowness with which crystallisation occurs. Further, if the fusion from the 42°- or 58°-acid is immersed in a mixture of ether and carbon dioxide or in liquid air, it forms an amorphous, glassy mass with a concave, funnel-shaped surface, and shows no tendency to crystallise, even after some hours; but if the mass is removed from the cooling mixture so that its temperature rises, the concavity of the surface gradually disappears, and it undergoes a usually sudden and always rapid crystallisation, the 58°-acid invariably separating, so that these two labile acids, which in the fused condition are optically identical, can be mutually interconverted without any seeding being necessary.

Results similar to the above were obtained on cooling the fused 68°-acid in ice and salt, ether and carbon dioxide, or liquid air, the only divergence being that occasionally, in additton to the 42°- or 58°-acid, the 68°-acid also separated.

Optical identity (compare preceding abstract) of these three acids does not, therefore, always present itself, and the conclusion is drawn that there are in reality two chemically different isomeric acids: (1) monomorphous *allo*cinnamic acid, m. p. 68°, and (2) dimorphous *iso*cinnamic acid, m. p. 42° and 58°. T. H. P.

Oxidation of *allo*-Cinnamylideneacetic Acid. C. N. Riiber (*Ber.*, 1911, **44**, 2389—2391).—Doebner (Abstr., 1890, 1274) has shown that cinnamylideneacetic acid, when cautiously oxidised with potassium permanganate, is converted into benzoic acid and racemic acid. It is now shown that *allo*-cinnamylideneacetic acid,

$$CHPh:CH\cdot CH:CH\cdot CO_2H,$$

under similar conditions is converted into benzoic acid and mesotartaric acid. The two cinnamylideneacetic acids are accordingly related in the same manner as fumaric and maleic acids, the isomerism being due to the double linking 1:2. The double linking 3:4 is hardly concerned, since both isomerides when distilled with quinoline give the same stable phenylbutadiene. E. F. A.

Reaction between Organomagnesium Compounds and Cinnamylidene Esters. III. Reactions with the Isomeric Methyl Esters of Cinnamylideneacetic Acid. Grace P. Reynolds (*Amer. Chem. J.*, 1911, **46**, 198—211. Compare Abstr., 1907, i, 852; 1908, i, 988).—The action of magnesium alkyl or aryl

bromides on the isomeric methyl cinnamylideneacetates may give rise to three different classes of compounds: (i) tertiary alcohols,

$$CHPh\!:\!CH\cdot CH\!:\!CH\cdot CR_2\cdot OH,$$

formed by replacement of the methoxy-group and addition of the magnesium compound to the carbonyl group; (ii) unsaturated ketones, $CHPh\!:\!CH\cdot CHR\cdot CH_2\cdot COR$, produced by 1:4-addition and simultaneous replacement of the methoxy-group; (iii) unsaturated esters of the type $CHPh\!:\!CH\cdot CHR\cdot CH_2\cdot CO_2Me$, formed by 1:4-addition only. It is found that the nature of the product depends on the magnesium compound employed. Whilst magnesium phenyl bromide forms only an unsaturated ketone and magnesium ethyl bromide a tertiary alcohol, the action of magnesium benzyl bromide yields a mixture of compounds belonging to all three classes.

Methyl allo*cinnamylideneacetate*, $CHPh\!:\!CH\cdot CH\!:\!CH\cdot CO_2Me$, obtained by the action of methyl alcohol and hydrogen chloride on the corresponding acid, is a liquid, which solidifies at $-15°$ to a white, crystalline mass, and is partly converted into the isomeric ester by distillation under diminished pressure. Both esters react with magnesium phenyl bromide, yielding β-phenyl-β-styrylpropiophenone (Kohler, Abstr., 1905, i, 258), which is converted by the further action of magnesium phenyl bromide into *αγεε-tetraphenyl-Δ^α-penten-ε-ol*,

$$CHPh\!:\!CH\cdot CHPh\cdot CH_2\cdot CPh_2\cdot OH.$$

The latter compound forms slender, white needles, m. p. 134°, and is oxidised by potassium permanganate to benzoic acid and *αγγ-triphenyl-γ-butyrolactone*, $\begin{array}{l}CHPh\cdot CO\\ |\\ CH_2\cdot CPh_2\end{array}\!\!>\!O$, which crystallises in long, iridescent needles, m. p. 157°. Experiments carried out with the isomeric methyl cinnamylideneacetates under similar conditions showed that the *allo*-ester reacts with magnesium phenyl bromide more readily than the isomeride.

The interaction of magnesium benzyl bromide and methyl cinnamylideneacetate yields (1) *αζ-diphenyl-γ-benzyl-Δ^α-hexen-ε-one*,

$$CHPh\!:\!CH\cdot CH(C_7H_7)\cdot CH_2\cdot CO\cdot CH_2Ph,$$

which is a viscid, lemon-yellow liquid, b. p. 265°/15 mm., and yields a *dibromide*, $C_{26}H_{24}OBr_2$, m. p. 165·5°; (2) *αζ-diphenyl-ε-benzyl-Δ^{αγ}-hexadien-ε-ol*, $CHPh\!:\!CH\cdot CH\!:\!CH\cdot C(CH_2Ph)_2\cdot OH$, a mobile, lemon-yellow liquid, b. p. 200°/10 mm.; the *tetrabromide* forms slender needles, m. p. 227° (decomp.); (3) *β-benzyl-γ-benzylidenebutyric acid*,

$$CHPh\!:\!CH\cdot CH(C_7H_7)\cdot CH_2\cdot CO_2H,$$

which crystallises in heavy, iridescent plates, m. p. 144°, yields a crystalline *methyl* ester, m. p. 66°, and is oxidised by potassium permanganate in aqueous sodium carbonate solution to benzoic and benzylsuccinic acids.

α-Phenyl-ε-ethyl-Δ^{αγ}-heptadien-ε-ol, $CHPh\!:\!CH\cdot CH\!:\!CH\cdot CEt_2\cdot OH$, obtained by the action of magnesium ethyl bromide on methyl cinnamylideneacetate, is a pale yellow, mobile liquid, b. p. 169°/10 mm. It is accompanied by a viscid liquid, b. p. 278—285°/10 mm., which deposits an *ester*, crystallising in needles, m. p. 136°, when kept. Hydrolysis of the latter substance with alcoholic potassium hydroxide yields an acid, m. p. 230°. The constitution of the last-mentioned substances has not been determined.

F. B.

Reaction between Unsaturated Compounds and Organic Zinc Compounds. II. ELMER P. KOHLER, GERTRUDE L. HERITAGE, and A. L. MACLEOD (*Amer. Chem. J.*, 1911, **46**, 217—236).—It has been shown previously (Abstr., 1910, i, 484) that the zinc compounds of esters of bromoacetic acid react with $\alpha\beta$-unsaturated ketones, yielding unsaturated hydroxy-acids, and from this the conclusion was drawn that the addition of organo-zinc compounds occurs only in the 1 : 2-position. The present paper deals with the interaction of phenyl styryl ketone and the zinc derivatives of the methyl or ethyl esters of α-bromopropionic, α-bromobutyric, α-bromo*iso*butyric, and bromomalonic acids. It is found that both 1 : 2- and 1 : 4-addition may take place with the formation of the compounds :

(I) $CHPh{:}CH{\cdot}CPh(O{\cdot}ZnBr){\cdot}CHR{\cdot}CO_2R'$ and
(II) $ZnBr{\cdot}O{\cdot}CPh{:}CH{\cdot}CHPh{\cdot}CHR{\cdot}CO_2R'$,

the relative proportions of the two products depending on the nature of the bromo-ester, $CHRBr{\cdot}CO_2R'$, employed.

When decomposed with acids, the zinc compounds of the first type yield esters of unsaturated hydroxy-acids,

$$CHPh{:}CH{\cdot}CPh(OH){\cdot}CHR{\cdot}CO_2R',$$

whilst those belonging to the second type give rise to esters of ketonic acids of the formula : $COPh{\cdot}CH_2{\cdot}CHPh{\cdot}CHR{\cdot}CO_2R'$. The zinc compounds produced by 1 : 4-addition may also yield unsaturated lactones, according to the scheme :

$$\begin{array}{l} CHPh{\cdot}CH{=}{=}CPh \\ \vert \qquad\qquad\quad \vert \\ CHR{\cdot}CO_2R' \quad O{\cdot}ZnBr \end{array} \longrightarrow \begin{array}{l} CHPh{\cdot}CH{:}CPh \\ \vert \qquad\qquad\ \vert \\ CHR{\cdot}CO{-}O \end{array} + OR'{\cdot}ZnBr.$$

The relative amounts of the products formed by 1 : 2- and 1 : 4-addition were determined by heating the mixtures with aqueous sodium carbonate, whereby the lactones and ketonic esters are converted into the sodium salts of the corresponding ketonic acids, whilst the unsaturated hydroxy-esters remain practically unchanged. The results thus obtained were as follows, the value first given being the percentage of the product formed by 1 : 2-addition : methyl α-bromoacetate, 100%, 0% ; methyl α-bromopropionate, 55%, 45% ; methyl α-bromobutyrate, 50%, 50% ; methyl α-bromo*iso*butyrate and methyl bromomalonate, 0%, 100%.

In several cases no reaction occurred when the bromo-esters were heated with zinc and the unsaturated ketone in benzene solution. The reaction is, however, readily induced by the addition of a small quantity of the copper salt of ethyl acetoacetate, or of other copper compounds which are soluble in benzene.

The action of zinc on methyl bromoacetate and phenyl styryl ketone has been re-investigated, and the product, after removal of methyl β-hydroxy-β-phenyl-α-benzylidenebutyrate, carefully examined for methyl benzoylphenylbutyrate, which would be formed by a 1 : 4-addition, but no evidence of its presence could be obtained. Methyl β-hydroxy-β-phenyl-γ-benzylidenebutyrate decomposes below 180° into methyl acetate and phenyl styryl ketone ; a similar decomposition into potassium acetate and phenyl styryl ketone takes place on treating the ester with alcoholic potassium hydroxide. When hydrolysed with aqueous sodium carbonate, it yields the corresponding *acid*, $CHPh{:}CH{\cdot}CPh(OH){\cdot}CH_2{\cdot}CO_2H$, which crystallises in colourless needles,

m. p. 147° (decomp.). When warmed with a small quantity of hydrochloric acid, the hydroxy-ester is converted into a viscid oil, which is hydrolysed by alcoholic potassium hydroxide to *β-phenylcinnamylideneacetic acid*, $CHPh{:}CH{\cdot}CPh{:}CH{\cdot}CO_2H$; this forms pale yellow, slender needles, m. p. 145—146°.

The product obtained by the interaction of zinc, ethyl α-bromopropionate, and phenyl styryl ketone in benzene solution, when decomposed with hydrochloric acid and heated with aqueous sodium carbonate, yields a mixture of two stereoisomeric *ethyl β-hydroxy-β-phenyl-γ-benzylidene-α-methylbutyrates*,

$$CHPh{:}CH{\cdot}CPh(OH){\cdot}CHMe{\cdot}CO_2H,$$

which may be separated by repeated crystallisation from methyl alcohol. The less soluble isomeride crystallises in slender needles, m. p. 107°, instantly decolorises bromine at the ordinary temperature, and decomposes above its m. p. into ethyl propionate and phenyl styryl ketone. When warmed with alcoholic potassium hydroxide, it yields phenyl styryl ketone and potassium propionate. The stereoisomeride, which is produced only in small quantity, separates from alcohol in large, transparent prisms, m. p. 81°, and resembles the preceding compound in its chemical properties.

The alkaline solution from which the above esters were separated yields on acidification two stereoisomeric *γ-benzoyl-β-phenyl-α-methyl butyric acids*, $CH_2Bz{\cdot}CHPh{\cdot}CHMe{\cdot}CO_2H$, which are separated by crystallisation from ether and light petroleum. Of these isomerides, the one obtained in larger quantity crystallises in slender, feathery needles, m. p. 149°, and yield a *methyl* ester crystallising in needles, m. p. 68°; the *ethyl* ester has m. p. 41°. The stereoisomeric acid forms slender needles, m. p. 105°.

The product obtained by the action of zinc on methyl α-bromobutyrate and phenyl styryl ketone in benzene solution when decomposed with acids yields *methyl β-hydroxy-β-phenyl-γ-benzylidene-α-ethylbutyrate*,

$$CHPh{:}CH{\cdot}CPh(OH){\cdot}CHEt{\cdot}CO_2Me,$$

which crystallises in needles, m. p. 117°, and, when heated above its m. p., is resolved into methyl butyrate and phenyl styryl ketone. Decomposition of the product with aqueous sodium carbonate yields *γ-benzoyl-β-phenyl-α-ethylbutyric acid*, $CH_2Bz{\cdot}CHPh{\cdot}CHEt{\cdot}CO_2H$, which crystallises in needles, m. p. 181°, and yields a *methyl* ester, m. p. 95°.

The *lactone*, $CHPh{<}{\begin{matrix}CH{=}CPh\\ CMe_2{\cdot}CO\end{matrix}}{>}O$, obtained by the action of zinc on ethyl α-bromo*iso*butyrate and phenyl styryl ketone, forms long, colourless needles, m. p. 97°, and is readily hydrolysed by alcoholic potassium hydroxide to *γ-benzoyl-β-phenyl-αα-dimethylbutyric acid*, $CH_2Bz{\cdot}CHPh{\cdot}CMe_2{\cdot}CO_2H$, which crystallises in slender, white needles, m. p. 159—160°. The lactone is accompanied by the *ethyl* ester of the last-mentioned acid; this has m. p. 83°, and has also been prepared from the lactone and corresponding acid; the *methyl* ester has m. p. 92°.

γ-Bromo-γ-benzoyl-β-phenyl-αα-dimethylbutyric acid,

$$CHBzBr{\cdot}CHPh{\cdot}CMe_2{\cdot}CO_2H,$$

prepared by brominating the preceding ketonic acid in chloroform or

carbon tetrachloride solution, forms colourless needles, m. p. 186° (decomp.); the *methyl* ester, m. p. 125°, and *ethyl* ester, m. p. 131°, were prepared in a similar manner. When treated with aqueous sodium carbonate the bromo-acid yields two stereoisomeric *γ-benzoyl-β-phenyl-αα-dimethyl-γ-butyrolactones*, $\begin{array}{l}CHPh\text{---}CHBz \\ | \qquad\quad\;\; | \\ CMe_2{\cdot}CO{\cdot}O\end{array}$, which may be separated by extraction with methyl alcohol. The more soluble modification forms needles, m. p. 113°; the stereoisomeride separates from acetone in needles, having m. p. 173°. When dissolved in cold alcoholic potassium hydroxide and the resulting solution immediately acidified, both isomerides yield a mixture of two stereoisomeric *γ-hydroxy-γ-benzoyl-β-phenyl-αα-dimethylbutyric acids*,

$$OH{\cdot}CHBz{\cdot}CHPh{\cdot}CMe_2{\cdot}CO_2H.$$

The less fusible of these acids loses water so readily that it could not be obtained free from the lactone of m. p. 173°. The stereoisomeric acid, which forms the major portion of the mixture, separates from ether in needles, m. p. 126° (decomp.); when heated for several hours at 120°, it loses water and is converted into the lactone of m. p. 113°.

Methyl bromomalonate, prepared by the addition of the calculated amount of bromine to methyl malonate, is a colourless, mobile liquid, b. p. 145°/22 mm. It reacts with zinc and phenyl styryl ketone in benzene solution, yielding *methyl β-benzoyl-α-phenylethylmalonate*, $CH_2Bz{\cdot}CHPh{\cdot}CH(CO_2Me_2)_2$. The latter compound crystallises in large, colourless needles, m. p. 107°, and is hydrolysed by alcoholic potassium hydroxide to the corresponding acid (Vorländer, Abstr., 1897, i, 286), which loses carbon dioxide at 170°, yielding γ-benzoyl-β-phenylbutyric acid, m. p. 156°. The preceding ester is accompanied by a viscid liquid, which appears to be a lactonic ester; when hydrolysed with alcoholic potassium hydroxide, this yields the same acid as that obtained by the hydrolysis of methyl β-benzoyl-α-phenylethylmalonate. F. B.

Crystallographic Study of Potassium *p*-Hydroxybenzoate. Aristide Rosati (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 53—54).—This substance, prepared by Comanducci and Marcello (Abstr., 1903, i, 485), forms transparent, colourless crystals belonging to the triclinic system [$a:b:c = 0{\cdot}6471:1:1{\cdot}7936$]. R. V. S.

***o*-Nitrophenylglyoxylic Acid.** Gustav Heller [with Friedrich Frantz and Heinrich Jürgens] (*Ber.*, 1911, 44, 2418—2421).—*o*-Nitrophenylglyoxylic acid (compare Claisen and Shadwell, *Ber.*, 1879, 12, 350) is conveniently prepared by oxidation of *o*-nitromandelic acid (Heller and Amberger, Abstr., 1904, i, 416) with alkaline permanganate. It crystallises in colourless, obliquely cut prisms, m. p. 156—157°.

The *ethyl* ester forms crystals, m. p. 43—44·5°.

The acid is reduced by zinc dust and ammonia to anthroxanic acid; the ester when reduced by stannous chloride and hydrochloric acid is converted into *ethyl anthroxanate*; this crystallises in long, bushy needles, m. p. 64—65°.

Methyl anthroxanate forms crystalline bunches, m. p. 70°.

E. F. A.

Keto-enolic Tautomerism. V. Desmotropy of Methyl Benzoylacetate. KURT H. MEYER (*Ber.*, 1911, **44**, 2729—2732).—Methyl and ethyl benzoylacetate contain respectively 16·7% and 29·2% of enolic modification at the ordinary temperature.

If the methyl ester is dissolved in sodium hydroxide solution and precipitated by dilute sulphuric acid, both strongly cooled, the free enol separates as an oil which solidifies when vigorously shaken; the solid can be dried in an absolute vacuum, but it is soon converted into an oily mixture of enol and ketone. This behaviour is similar to that of *iso*phenylnitromethane. The enolic form or methyl β-hydroxy-cinnamate melts indefinitely at 30—40°, and solidifies again when rapidly cooled. The alcoholic solution is coloured intensely reddish-violet by ferric chloride, and also reacts quickly with *anti-p*-nitrobenzenediazonium hydroxide. The crystalline enol, after two hours' drying, contained 89·1% of the enolic form. In a state of equilibrium at 20°, the ester contained 14% of enol in acetic acid, 21% in alcohol, 56% in carbon disulphide, and 69% in hexane. These numbers are similar to those obtained with ethyl acetoacetate.

The values of the velocity constants at 0° in absolute alcohol are k_1 (ketonisation) = 0·10 and k_2 (enolisation) = 0·04. At the boiling point the alcoholic solution contains only about one-half as much enol as at 0°.

Unlike the equilibrium of ethyl acetoacetate, that of methyl benzoylacetate exhibits a distinct temperature-coefficient, the equilibrium being displaced towards the ketone by rise of temperature; the same is the case with acetylacetone, so that the independence of the equilibrium on the temperature is a constitutive property of ethyl acetoacetate. T. H. P.

Preparation of *m*-Hydroxy-β-phenylpropionic Acid Alkyl Ethers and their Salts. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P 234852).—*m-Ethoxy-β-phenylpropionic acid*, m. p. 52—53°, b. p. 205°/20 mm., can be prepared (1) by heating *m*-hydroxy-β-phenyl-propionic acid with ethyl bromide and sodium hydroxide in alcoholic solution at 120°; (2) by reducing *m*-ethoxycinnamic acid with sodium amalgam; or (3) by diazotising *m*-amino-β-phenylpropionic acid in an anhydrous solvent, isolating the diazonium sulphate with ether, and subsequently boiling it with absolute alcohol; the *sodium* salt forms a colourless powder.

m-*Propoxy-β-phenylpropionic acid* has m. p. 56—57° and b. p. 203—204°/15 mm. These compounds have antipyretic and anti-rheumatic properties. F. M. G. M.

New Reactions of Cyanogen and Acyl Cyanides. DANIEL VORLÄNDER [and, in part, A. FRIEDBERG, CH. VAN DER MERVE, L. ROSENTHAL, M. E. HUTH, and M. VON BODECKER] (*Ber.*, 1911, **44**, 2455—2476).—The interaction of cyanogen with benzene and its homologues, or with phenolic ethers, yields acyl cyanides, R·CO·CN, nitriles, R·CN, and diketones, R·CO·CO·R, together with more complex substances, the constitution of which has not been determined.

When cyanogen is passed into a mixture of benzene and aluminium chloride for one hour at the ordinary temperature, and the product decomposed with cold dilute hydrochloric acid, benzoyl cyanide is produced. If the mixture is boiled and the passage of cyanogen continued for four hours, the benzoyl cyanide is accompanied by benzonitrile (compare Desgrez, Abstr., 1896, i, 419). The product of the reaction always contains a certain amount of a tarry substance, which, on decomposition with acids, yields benzil. The latter compound forms the main product when a mixture of benzene and aluminium chloride is saturated with cyanogen and allowed to remain at the ordinary temperature for three days. In addition to the above compounds, several other substances are formed in the reaction, one of these being a blue dye, m. p. 145—148°.

With respect to the mechanism of the reaction, it is considered that the first stage consists in the formation of an imino-nitrile (I), which decomposes into benzonitrile and hydrogen cyanide, and on treatment with acids yields benzoyl cyanide, thus:

$$C_6H_6 + C_2N_2 \longrightarrow \text{(I) } CN{\cdot}CPh{:}NH \longrightarrow CN{\cdot}COPh\,;$$

the formation of benzil is due to the decomposition of a di-imino-compound (II), produced by the further condensation of the imino-nitrile with benzene:

$$CN{\cdot}CPh{:}NH + C_6H_6 = \text{(II) } NH{:}CPh{\cdot}CPh{:}NH.$$

The interaction of cyanogen, toluene, and aluminium chloride, under conditions similar to those given in the case of benzene, results in the formation of *p*-toluonitrile, *p*-toluic acid, *pp'*-dimethylbenzil, and *p*-methylbenzoyl cyanide (Söderbaum, Abstr., 1893, i, 159).

With ethylbenzene the product consists of p-*ethylbenzonitrile* and *p*-ethylbenzoic acid, together with p-*ethylbenzoyl cyanide*, which could not be isolated, and was therefore identified by conversion into *p*-ethylbenzanilide, m. p. 121°.

The only substance which could be identified in the product obtained from cyanogen and diphenyl was p-*phenylbenzoyl cyanide*.

The action of cyanogen and hydrogen chloride on a solution of phenetole in carbon disulphide in the presence of aluminium chloride yields p-*ethoxybenzoyl cyanide*, which has m. p. 43°, and is more readily prepared by heating *p*-ethoxybenzoyl chloride with mercuric cyanide at 125—130°; it gives a green, and finally blue, solution with strong sulphuric acid, and is decomposed by boiling with dilute hydrochloric acid into *p*-ethoxybenzoic acid and hydrogen cyanide; with aniline it yields *p*-ethoxybenzanilide (Leuckart, Abstr., 1890, 759).

p-*Ethoxyphenylglyoxylic acid*, obtained by the action of fuming hydrochloric acid on the preceding nitrile, crystallises with water in colourless prisms, m. p. 52°; the anhydrous acid is obtained by crystallisation from benzene, and has m. p. 125° (decomp.); it yields a *phenylhydrazone*, $C_{16}H_{16}O_3N_2$, long, yellow needles, m. p. 153° (decomp.), and an *azine*, crystallising in light yellow needles, which have m. p. 173—176°, and simultaneously lose carbon dioxide with the formation of *pp'*-diethoxybenzalazine; the *oxime* has m. p. 152—154° (decomp.).

pp'-*Diethoxybenzil*, $C_{18}H_{18}O_4$, prepared by the action of cyanogen and hydrogen chloride on a carbon disulphide solution of phenetole in the presence of aluminium chloride for three to four days, crystallises in

silvery-white, microscopic prisms, m. p. 149°, and gives a red coloration with concentrated sulphuric acid. It yields an *osazone*, crystallising in small, yellow plates, m. p. 171°, and is converted by alcoholic potassium hydroxide into pp′-*diethoxybenzilic acid*, which forms narrow prisms, m. p. 202°, with previous darkening.

p-Methoxybenzoyl cyanide, obtained from anisole in the usual manner, crystallises in colourless needles, m. p. 60°; Mauthner (Abstr., 1909, i, 160) gives 63—64°. It may also be prepared by the interaction of anisoyl chloride and mercuric cyanide; when warmed with acids or alkalis it yields anisic acid.

In view of the above-mentioned formation of benzil from the intermediate product, NH:CPh·CN, it was anticipated that the closely related benzoyl cyanide would condense with benzene to form benzil in a similar manner.

It was, however, found that benzoyl cyanide and benzene react at the ordinary temperature in the presence of aluminium chloride and hydrogen chloride, yielding 9-cyanofluorene (Wislicenus and Russ, Abstr., 1910, i, 839), which is converted by heating with fuming hydrochloric or hydriodic acid into 9-fluorenecarboxylic acid. On the other hand, when a mixture of benzene, benzoyl cyanide, and aluminium chloride is heated in carbon disulphide solution, triphenylacetonitrile (E. and O. Fischer, Abstr., 1879, 326, 385) is produced, thus: $CN{\cdot}COPh + 2C_6H_6 \longrightarrow CPh_3{\cdot}CN + H_2O$.

A number of substituted derivatives of triphenylacetonitrile has been prepared in a similar manner.

Phenyldi-p-*tolylacetonitrile*, $C_{22}H_{19}N$, obtained from benzoyl cyanide and toluene, crystallises in apparently monoclinic prisms, m. p. 132—133°, and is converted by the action of sodium on its alcoholic solution into phenyldi-*p*-tolylmethane (Kliegl, Abstr., 1905, i, 186); it may also be prepared by heating ω-chlorophenyldi-*p*-tolylmethane (Gomberg, Abstr., 1904, i, 489) with mercuric cyanide.

4 : 4′-*Diethyltriphenylacetonitrile*, $C_{24}H_{23}N$, prepared from ethylbenzene and benzoylcyanide, crystallises in colourless plates, m. p. 111—112°.

4 : 4′-*Dimethoxytriphenylacetonitrile*, $C_{22}H_{19}O_2N$, obtained from anisole, crystallises in short, colourless, rods, m. p. 98°; it is also obtained in small yield by the interaction of ω-chloro-4 : 4′-dimethoxytriphenylmethane and mercuric cyanide. When reduced with sodium in alcoholic solution, it yields 4 : 4′-dimethoxytriphenylmethane (Baeyer and Villiger, Abstr., 1902, i, 380).

4 : 4′-*Dihydroxytriphenylacetonitrile*, $C_{20}H_{15}O_2N$, prepared by boiling the preceding nitrile with hydriodic acid, forms colourless, hexagonal leaflets, m. p. 202°; it is converted by the action of methyl sulphate in alkaline solution into the original nitrile; the *diacetyl* derivative crystallises in colourless leaflets, m. p. 130°. When boiled with phosphorus and hydriodic acid, 4 : 4′-dimethoxytriphenylacetonitrile yields 4-hydroxydiphenylacetic acid (Bistrzycki and Flatau, Abstr., 1897, i, 190), which forms an *ethyl* ester, crystallising in stellar aggregates of prisms, m. p. 92°; the *methyl* ester is an oil.

4-*Methoxytriphenylacetonitrile*, prepared from anisoyl cyanide and benzene, crystallises in colourless plates or white needles, m. p. 137°.

4 : 4′-*Diethoxytriphenylacetonitrile*, obtained from benzoyl cyanide and phenetole, forms short, pointed prisms, m. p. 120° ; it is converted by heating with hydriodic acid into 4 : 4′-dihydroxytriphenylacetonitrile and 4-hydroxydiphenylacetic acid.

Cyanogen and sulphurous acid react slowly in aqueous solution, yielding hydrogen cyanide and sulphuric acid :

$$C_2N_2 + H_2SO_3 + H_2O = 2HCN + H_2SO_4.$$

F. B.

Condensation of *p*- and *o*-Methoxymandelonitriles with Phenols and Phenolic Ethers. AUGUSTIN BISTRZYCKI, J. PAULUS, and R. PERRIN (*Ber.*, 1911, **44**, 2596—2617).—The paper contains merely a description of the following substances, and has been published in consequence of Stoermer and Hildebrandt's recent work (this vol., i, 664).

o- and *p*-Methoxymandelonitriles condense like the corresponding acids with phenols or phenolic ethers in the presence of 73% sulphuric acid, yielding nitriles of the type $OMe{\cdot}C_6H_4{\cdot}CHAr{\cdot}CN$; thus anisaldehydecyanohydrin (1 mol.) and phenol ($2\frac{1}{3}$ mols.) yield 4-*hydroxy*-4′-*methoxydiphenylacetonitrile*, $OMe{\cdot}C_6H_4{\cdot}CH(CN){\cdot}C_6H_4{\cdot}OH$, prismatic needles, m. p. 175—176° (erroneously described by Stoermer and Hildebrandt as the lactone of *o*-hydroxyphenylanisylacetic acid), which forms an *acetyl* derivative, m. p. 85·5—86·5°, and is hydrolysed by boiling alcoholic potassium hydroxide, forming 4-*hydroxy*-4′-*methoxydiphenylacetic acid* (p-*hydroxyphenylanisylacetic acid*), m. p. 148·5—149·5°. This acid does not yield a lactone (consequently the hydroxyl group is assumed to be in the para-position), and evolves two-thirds of the theoretical quantity of carbon monoxide when heated with concentrated sulphuric acid at 170° (compare Bistrzycki and Siemiradzki, Abstr., 1908, i, 635). Anisaldehydecyanohydrin and *o*-cresol yield in a similar manner 4-*hydroxy*-4′-*methoxy*-3-*methyldiphenylacetonitrile*, m. p. 142—143° (*acetyl* derivative, m. p. 74·5—76°) ; the corresponding *acid*, m. p. 128—129°, loses two-thirds of the theoretical quantity of carbon monoxide with sulphuric acid at 100—120°. The lactone of *p*-hydroxytolylanisylacetic [2-hydroxy-4′-methoxy-5-methyldiphenylacetic] acid (Stoermer and Hildebrandt, *loc. cit.*) is hydrolysed by 6% potassium hydroxide to the corresponding *acid*, m. p. 140° (decomp.), which exhibits considerable stability for a γ-lactone. The lactone is converted into 2-*hydroxy*-4′-*methoxy*-5-*methyldiphenylacetamide*, decomp. 137·5°, by 25% aqueous ammonia and a little alcohol, and into the *hydrazide*, $OMe{\cdot}C_6H_4{\cdot}CH(CO{\cdot}NH{\cdot}NH_2){\cdot}C_6H_3Me{\cdot}OH$, decomp. 182·5° (*benzylidene* derivative, m. p. 184°), in boiling alcohol by 50% aqueous hydrazine hydrate.

Anisaldehydecyanohydrin and catechol condense to form 3 : 4-*dihydroxy*-4′-*methoxydiphenylacetonitrile*,

$$OMe{\cdot}C_6H_4{\cdot}CH(CN){\cdot}C_6H_3(OH)_2,$$

m. p. 153·5—154·5°, darkening at 130° (*diacetate*, m. p. 77—78°), which develops a blue, and by warming a bluish-violet, coloration with concentrated sulphuric acid. Anisaldehydecyanohydrin and β-naphthol yield the *lactone* of 2-*hydroxy*-α(?)-*naphthyl*-4-*methoxyphenyl*-

acetic acid, $OMe\cdot C_6H_4\cdot CH<\substack{CO—\\C_{10}H_6}>O$, m. p. 145—146° (decomp.), long, prismatic needles.

Anisaldehydecyanohydrin condenses very readily with anisole to form *dianisylacetonitrile* [4 : 4′-*dimethoxyphenylacetonitrile*],

$$CN\cdot CH(C_6H_4\cdot OMe)_2,$$

m. p. 154·5°. Dianisylacetic acid reacts readily with phosphorus pentachloride and phosphoryl chloride to form the *chloride*, $CH(C_6H_4\cdot OMe)_2\cdot COCl$, m. p. 58—61°. In a similar manner phenetole yields *anisylphenetylacetonitrile*, m. p. 87—88°, whilst veratrole yields 3 : 4 : 4′-*trimethoxydiphenylacetonitrile*, m. p. 96°, the corresponding *acid* having m. p. 154—155°.

o-Anisaldehydecyanohydrin (rhombic crystals, $a:b:c = 0{\cdot}862:1:0{\cdot}462$) condenses less readily than the para-isomeride with phenols, except *p*-cresol. The *lactone* of 2-*hydroxy*-2′-*methoxy*-5-*methyldiphenylacetic acid*, $OMe\cdot C_6H_4\cdot CH<\substack{CO——\\C_6H_3Me}>O$, m. p. 136°, obtained directly from the cyanohydrin and *p*-cresol with 73% sulphuric acid on the water-bath, is hydrolysed to the *acid*, $C_{16}H_{16}O_4,H_2O$, m. p. 150°, by 6% potassium hydroxide, to the *amide*, $C_{16}H_{17}O_3N$, decomp. 177—178°, by alcoholic ammonia at 100°, to the *anilide*, m. p. 192—194°, by distillation with aniline, and to the *hydrazide*, m. p. 154° (*benzylidene* derivative, m. p. 202°), by hydrazine hydrate.

The condensation of *o*-anisaldehydecyanohydrin and *o*-cresol yields a mixture of 4-*hydroxy*-2′-*methoxy*-3-*methyldiphenylacetamide* (prisms containing $C_2H_4O_2$, m. p. 130—131°, from acetic acid) and the *lactone* of 4-*hydroxy*-2′-*methoxy*-3-*methyldiphenylacetic acid*, m. p. 164°. The cyanohydrin and phenol likewise yield a mixture of the *lactone* of 2-*hydroxy*-2′-*methoxydiphenylacetic acid*, m. p. 160—162°, and 4-*hydroxy*-2′-*methoxydiphenylacetamide*, m. p. 204—205°, which is hydrolysed only slowly and incompletely by boiling concentrated potassium hydroxide. C. S.

Diphenyl Derivatives. FRITZ MAYER (*Ber.*, 1911, **44**, 2298—2305).—The following substances were obtained in the course of attempts to synthesise pyrene by using Ullmann's method for the preparation of *s*-diphenyl derivatives (Abstr., 1901, i, 586).

2-Acetylamino*iso*phthalic acid, prepared by Noelting and Gachot's method (Abstr., 1906, i, 181), is best purified by heating with acetic anhydride, which gives rise to the corresponding *acetylanthranil*, m. p. 217—218°; the latter is readily re-converted into the acid by crystallisation from water. The acid softens at 195—200° and decomposes at 205—206°, and when warmed with diluted sulphuric acid yields 2-amino*iso*phthalic acid. The latter, on diazotisation and treatment with iodine in potassium iodide solution, gives 2-*iodo* iso*phthalic acid*, m. p. 205—222° (decomp.), with some of the corresponding hydroxy-acid, from which it is best separated by conversion into the *methyl* ester, m. p. 50°, long, colourless needles. The latter, when heated with copper powder at 140—150°, yields *diphenyl*-2 : 6 : 2′ : 6′-*tetracarboxylic acid*, iridescent leaflets, melting above 350°, in the form of the *tetramethyl* ester, m. p. 125—126°, which crystallises

in colourless needles. The corresponding *acid chloride*, $C_{16}H_6O_4Cl_4$, m. p. 189—190°, obtained as a brittle mass by precipitation with light petroleum from benzene, does not yield pyrene on reduction with the usual agents, and when heated with copper gives an amorphous, red substance.

2-*Iodo*-m-*toluic acid*, m. p. 145—146°, prepared from the corresponding methyl aminotoluate (Müller, Abstr., 1909, i, 159) by diazotising, adding potassium iodide, and hydrolysing the *methyl* ester, b. p. 280—290°, so obtained, crystallises in needles from benzene or methyl alcohol. When heated with copper powder at 220°, it yields 2 : 2′-*dimethyldiphenyl*-6 : 6′-*dicarboxylic acid*, which crystallises from ether on addition of light petroleum, sinters strongly, and finally melts at 230°. The yield is small.

Methyl o-*iodocinnamate*, m. p. 65°, crystallises in silky, yellow needles, and does not yield pyrene when heated with copper powder.

o-Iodobenzaldehyde may be readily identified by condensing it with aniline, when it yields o-*iodobenzylideneanilene*, m. p. 75—76°, crystallising from methyl alcohol in colourless needles. When heated with copper powder at 210—220°, *o*-iodobenzaldehyde furnishes 2 : 2′-*dialdehydodiphenyl* as a viscous, brown oil with an odour similar to that of benzaldehyde; the *dioxime*, m. p. 175—176°, crystallises from methyl alcohol in yellow needles. The dialdehyde, when heated with acetic anhydride and sodium acetate, is converted into *diphenyl*-2 : 2′-*diacrylic acid*, m. p. 286° (decomp.), which crystallises from acetic acid, yields diphenic acid on oxidation with dilute alkaline permanganate, and when distilled alone or with lime, lead oxide, or zinc dust, gives an oily substance which slowly deposits a small amount of crystalline matter from which a *picrate*, m. p. 140°, can be obtained. T. A. H.

Simultaneous Reduction and Oxidation by Catalysis. NICOLAI ZELINSKY and NIKOLAUS GLINKA (*Ber.*, 1911, **44**, 2305—2311*).—Methyl Δ^1-tetrahydroterephthalate, dissolved in dry ether, when treated with palladium black in presence of a current of hydrogen at atmospheric temperature furnishes a mixture of methyl terephthalate and methyl *cis*-hexahydroterephthalate. The same change takes place, but more slowly, with platinum black. The oxidation is not due to oxygen occluded by palladium, since it does not occur in absence of hydrogen. The mechanism of the reaction may be that the tetrahydroterephthalate is immediately reduced in part by the palladium in virtue of hydrogen occluded by the latter, the hydrogen thus lost by the palladium being recovered from the residual tetrahydroterephthalate, so that a re-distribution of the hydrogen in 3 mols. of the tetrahydroterephthalate occurs thus: $3C_{10}H_{14}O_4 = 2C_{10}H_{16}O_4 + C_{10}H_{10}O_4$; or, as suggested by Bach (Abstr., 1910, ii, 31), a labile palladium perhydride may be formed, which reacts with an oxyperhydride, OH_4, momentarily formed, in which, under the influence of palladium perhydride, the normal affinity of oxygen in the molecule of water is so distributed as to hold 4H in place of 2H. The existence of such an intermediate product would explain (1) the simultaneous occurrence of oxidation and reduction in

* and *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1084—1091.

this instance; (2) Ipatieff's observation that in catalytic reduction at high pressures the presence of oxygen favours the action, and (3) that in Sabatier's nickel reduction method, nickel prepared at 200—250°, at which temperature it may still contain oxygen, gives the best results. The palladium black used in these experiments was obtained by adding first formic acid and then alkali to an aqueous solution of palladium ammonium chloride. T. A. H.

[Preparation of Dichloro-*o*-carboxyphenylthiolacetic Acid.] KALLE & Co (D.R.-P. 234375).—When the di- or tri-halogenated *o*-carboxyphenylthiolacetic acid neutral esters are treated with sodium hydroxide, they yield the corresponding halogenated oxythionaphthencarboxylic acid esters, which are then hydrolysed and the resulting product oxidised to dyes.

Dichloro-o-carboxyphenylthiolacetic acid, $CO_2H \cdot C_6H_2Cl_2 \cdot S \cdot CH_2 \cdot CO_2H$, glistening, colourless needles, was prepared as follows: Aceto-*o*-toluidide was dichlorinated, oxidised with potassium permanganate to dichloroacetylanthranilic acid, the acetyl group eliminated, and the dichloroanthranilic acid so obtained, diazotised and converted into either a dichloro-*o*-thiolbenzoic acid or a xanthate derivative, which on subsequent treatment with chloroacetic acid yielded the foregoing acid. Esterification was carried out in the usual way, and the ring subsequently closed by heating at 40—50° with concentrated sodium hydroxide, yielding *ethyl dichloro-3-oxy-(1)-thionaphthencarboxylate*, which was not isolated but hydrolysed by dilution and prolonged boiling. Subsequent oxidation with potassium ferricyanide (or air) furnished a dye which was isolated as a dark violet powder. F. M. G. M.

Action of Organo-magnesium Compounds on 4-Methoxyphthalic Anhydride. HUGO BAUER (*Arch. Pharm.*, 1911, **249**, 450—453).—It has been shown previously (Abstr., 1908, i, 274) that the nitro-group in nitrodiethylphthalide (Abstr., 1904, i, 417) probably occupies position 5, and to confirm this an attempt was made to synthesise 5-methoxydiethylphthalide, which was prepared from the nitro-compound as described already (Abstr., 1908, i, 274). By the action of magnesium ethyl bromide on 4-methoxyphthalic anhydride, either 4- or 5-methoxydiethylphthalide might be formed, and trial proved that the former only was produced.

4-*Methoxydiethylphthalide*, $OMe \cdot C_6H_3 < \substack{CEt_2 \\ CO} > O$, m. p. 86—87°, crystallises from dilute alcohol in colourless prisms. On fusion with potassium hydroxide, it furnishes anisic acid, and on nitration gives only a *mononitro*-derivative, m. p. 117°, which crystallises from alcohol in faintly yellow needles. On reduction with iron and acetic acid at 100°, this gives the corresponding *amino*-compound, m. p. 163°, which crystallises from dilute alcohol in colourless leaflets or prisms. It fluoresces blue in alcohol solution. T. A. H.

Action of Organo-magnesium Compounds on Homophthalic Anhydride. HUGO BAUER and EWALD WÖLZ (*Arch. Pharm.*, 1911, **249**, 454—458. Compare Abstr., 1904, i, 417; 1905, i, 210; 1909, i, 585, and preceding abstract).—The previous work (*loc. cit.*)

has shown that the normal action between organo-magnesium compounds and dicarboxylic anhydrides gives rise to dialkylphthalides, but in certain cases other reactions occur, such as the formation of *o*-diketones or the production of monoalkylphthalides. This condensation has therefore been further investigated with homophthalic anhydride in place of phthalic anhydride. The former may give rise to dialkyl derivatives of either type represented by the formulæ:

$$C_6H_4<\begin{matrix}CR_2\cdot O \\ CH_2\cdot CO\end{matrix} \quad \text{or} \quad C_6H_4<\begin{matrix}CH_2\cdot CR_2 \\ CO\text{—}O\end{matrix}.$$

The former type should yield on fusion with potassium hydroxide, and assuming R to be Me, acetone and phenylacetic acid, whilst the second should give acetone and *o*-toluic acid. Application of this reaction to the condensation products gave unexpected results, so that at present constitutional formulæ cannot be assigned to them.

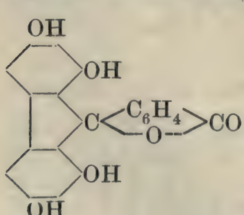
Dimethylhomophthalide, $C_{11}H_{12}O_2$, m. p. 94—95°, obtained by condensing magnesium methyl iodide with homophthalic anhydride and treating the product with dilute acid, crystallises from hot ether in slender, colourless needles, dissolves in warm alkalis, and is re-precipitated by acids, does not react with hydroxylamine or ammonia, and fluoresces green when warmed with sulphuric acid.

Diphenylhomophthalide, $C_{21}H_{16}O_2$, m. p. 160—161°, similarly prepared, crystallises from alcohol, and resembles the foregoing substance in properties, but gives an orange-red to brownish-red coloration with sulphuric acid.

Dibenzylhomophthalide, $C_{23}H_{20}O_2$, m. p. 163—164°, crystallises from alcohol, and gives a wine-red coloration with sulphuric acid.

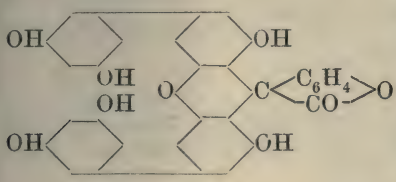
T. A. H.

Phthaleins of 3 : 5 : 3′ : 5′-Diresorcinol (3 : 5 : 3′ : 5′-Tetrahydroxydiphenyl). RICHARD MEYER and KARL MEYER (*Ber.*, 1911, **44**, 2678—2684).—The soluble phthalein obtained by Benedikt and Julius (Abstr., 1884, 1139; compare also Link, *ibid.*, 1881, 95) by the condensation of phthalic anhydride and 3 : 5 : 3′ : 5′-tetrahydroxydiphenyl in the presence of concentrated sulphuric acid has, according to the authors, the annexed constitution.



When warmed with acetic anhydride and a little sulphuric acid, it yields a *tetra-acetate*, which forms long, flat, rhomb-shaped crystals, m. p. 237—238°; the *tetrabenzoate* crystallises in stout, prismatic needles, m. p. 180—181°. The *tetramethyl ether*, $C_{20}H_8O_2(OMe)_4$, obtained by the action of methyl sulphate in alkaline solution, forms colourless needles; the *tetraethyl ether*, prepared by alkylating the phthalein either with ethyl iodide and sodium ethoxide in alcoholic solution, or by means of ethyl sulphate in alkaline solution, crystallises in flat needles or leaflets, m. p. 223°. When brominated in glacial acetic acid solution the phthalein yields a *tribromo*-derivative, $C_{20}H_9O_6Br_3$, crystallising in slender needles.

The insoluble phthalein, obtained by Benedikt and Julius (*loc. cit.*), is best prepared by the condensation of 1 mol. of phthalic anhydride with 2 mols. of 3 : 5 : 3′ : 5′-tetrahydroxydiphenyl in the presence of concentrated sulphuric acid at 120°. It has no m. p., dissolves in alkalis with a blue coloration, and is considered to be a hexahydroxydiphenylfluoran of the annexed constitution. It yields a *hexabenzoate*, crystallising in broad leaves, m. p. 245—250°; the *hexaethyl ether*, prepared by means of ethyl sulphate, crystallises in needles, m. p. 234—236°.



4 : 4′-(or 2 : 2′-)-*Bisbenzeneazo*-3 : 5 : 3′ : 5′-*tetrahydroxydiphenyl*,

$$NPh{:}N{\cdot}C_6H_2(OH)_2{\cdot}C_6H_2(OH)_2{\cdot}N{:}NPh,$$

obtained by the combination of benzenediazonium chloride and 3 : 5 : 3′ : 5′-tetrahydroxydiphenyl in alkaline solution, crystallises in stout, red needles having a steel-blue lustre.

4 : 4′-(or 2 : 2′-)-*Bis*-p-*tolueneazo*-3 : 5 : 3′ : 5′-*tetrahydroxydiphenyl*,

$$C_{12}H_8O_4(N_2{\cdot}C_7H_7)_2,$$

prepared in a similar manner, forms slender, red needles. F. B.

Synthesis of Chrysene. Erich Beschke [with Mariam Winograd-Finkel and Georg Köhres] (*Annalen*, 1911, **384**, 143—172).—The interaction of benzil, ethyl bromoacetate, and zinc in boiling benzene leads to the formation of the racemic and meso-modifications, m. p. 137° and 168° respectively, of *ethyl βγ-dihydroxy-βγ-diphenyladipate*, $CO_2Et{\cdot}CH_2{\cdot}CPh(OH){\cdot}CPh(OH){\cdot}CH_2{\cdot}CO_2Et$, which are separated by the insolubility of the latter in cold benzene. When boiled with acetic and concentrated hydrochloric acids, or heated above its m. p., the racemic modification is easily converted into the *di-lactone*, $CO<\genfrac{}{}{0pt}{}{O\text{——}CPh{\cdot}CH_2}{CH_2{\cdot}CPh\text{——}O}>CO$, m. p. 194°, which is being examined.

The meso-modification forms a *diacetyl* derivative, m. p. 171°, and is hydrolysed by boiling 10% sodium hydroxide, yielding the *sodium* salt, $C_{18}H_{16}O_6Na_2,10H_2O$, from which a stable, sparingly soluble *silver* salt, $C_{18}H_{16}O_6Ag_2,3H_2O$, has been prepared. The anhydrous silver salt is converted into silver, carbon dioxide, and acetophenone by distillation, and regenerates the meso-ester with ethyl iodide. *βγ-Dihydroxy-βγ-diphenyladipic acid*, m. p. 205°, obtained from the sodium salt and dilute acetic acid, is converted by alcoholic hydrogen chloride, not into the original meso-ester, but into *ethyl β-hydroxy-βγ-diphenylbutyrolactone-γ-acetate* [3-*hydroxy*-5-*keto*-2 : 3-*diphenyltetrahydrofuran*-2-*acetate*], $CO_2Et{\cdot}CH_2{\cdot}CPh<\genfrac{}{}{0pt}{}{CPh(OH){\cdot}CH_2}{\text{————————}O}>CO$, m. p. 138°, which is also obtained by adding a little concentrated hydrochloric acid to a boiling concentrated solution of the meso-ester in glacial acetic acid. *β-Hydroxy-βγ-diphenylbutyrolactone-γ-acetic acid*, $C_{18}H_{16}O_5$, m. p. 179°, is obtained by the action of acetic acid and a mineral acid on its ethyl

ester or on βγ-dihydroxy-βγ-diphenyladipic acid, but by too prolonged action the former method yields *βγ-diphenylcrotonolactone-γ-acetic* [*5-keto-2 : 3-diphenyl-2 : 5-dihydrofuran-2-acetic*] *acid*,

$$CO_2H\cdot CH_2\cdot CPh{<}\begin{matrix}CPh{:}CH \\ | \\ O\text{——}CO\end{matrix},$$

m. p. 184°. This acid, however, in the form of its *ethyl* ester, m. p. 94°, is more easily obtained by treating the above-mentioned meso-ester in acetic anhydride with concentrated sulphuric acid below 40—50°.

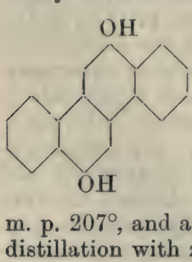
When ethyl βγ-diphenylcrotonolactone-γ-acetate is treated with boiling alcoholic sodium hydroxide (not in excess), the sodium salts of two acids are obtained. One of these acids is the *monoethyl* ester of βγ-diphenylmuconic acid, $CO_2H\cdot CH{:}CPh\cdot CPh{:}CH\cdot CO_2Et$, m. p. 140°, which lactonises to the original ester when boiled with acetic acid. The other acid is βγ-diphenylmuconic acid, which, however, cannot be isolated, since it at once changes to βγ-diphenylcrotonolactone-γ-acetic acid when liberated from its sodium salt. *Diethyl βγ-diphenylmuconate*, m. p. 72°, obtained from the silver salt of either of the two acids and ethyl iodide, reacts with bromine in chloroform in sunlight to form a *substance*, $C_{20}H_{17}O_4Br$, m. p. 143°, which probably has the constitution

$$CO_2Et\cdot CHBr\cdot CPh{<}\begin{matrix}CPh{:}CH \\ | \\ O\text{——}CO\end{matrix}.$$

When aqueous sodium βγ-diphenylmuconate is treated with iodine in potassium iodide and the solution is acidified after prolonged keeping, *βγ-diphenylcrotonolactone-γ-iodoacetic acid*,

$$CO_2H\cdot CHI\cdot CPh{<}\begin{matrix}CPh{:}CH \\ | \\ O\text{——}CO\end{matrix},$$

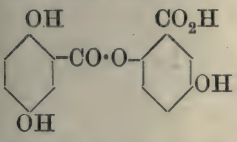
m. p. 217°, is obtained, which is reduced by zinc and acetic acid to *βγ-diphenyl-αδ-dihydromuconic acid*, $CO_2H\cdot CH_2\cdot CPh{:}CPh\cdot CH_2\cdot CO_2H$, m. p. 297°. This acid is best obtained by reducing sodium diphenylmuconate with sodium amalgam, whereby an *acidic* by-product, $C_{18}H_{16}O_4$, m. p. 195° (*ethyl* ester, m. p. 56°), is also formed, which is easily soluble in alcohol. Diphenyldihydromuconic acid forms an *ethyl* ester, m. p. 86°, and is converted by acetic anhydride and concentrated sulphuric acid into the *di-acetate*, m. p. 246°, of 2 : 8-*dihydroxychrysene* (annexed constitution), which is itself obtained by hydrolysing the diacetate by trituration with cold concentrated sulphuric acid. 2 : 8-Dihydroxychrysene yields yellow solutions in alkalis (becoming blue in the air), forms a *diethyl ether*, m. p. 207°, and a *dibenzoate*, m. p. 280°, and is reduced to chrysene by distillation with zinc dust.



C. S.

Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations. V. EMIL FISCHER and KARL FREUDENBERG (*Annalen*, 1911, 384, 225—244. Compare Abstr., 1910, i, 265).—Didepsides of the more important di- and tri-hydroxybenzoic acids have been prepared on account of their relation to many natural products.

Dimethylcarbonatodigentisic acid, $C_{18}H_{14}O_{11}$, m. p. 166—167° (corr.), colourless, flexible needles, is obtained by shaking a mixture of 5-methyl-carbonato-2-hydroxybenzoic acid, dimethylaniline, benzene, and phosphorus trichloride for three days at the ordinary temperature; its alcoholic solution develops a deep red coloration with ferric chloride.



Digentisic acid (annexed constitution), m. p. 208—209° (corr.), is obtained by hydrolysing the preceding compound by *N*-ammonia at 18—20° in an atmosphere of hydrogen. In contrast to gentisic acid, it precipitates dilute solutions of albumin or of quinine acetate, and develops a transient, blue coloration with ferric chloride. *Dimethylcarbonatodi-β-resorcylic acid*, $C_{18}H_{14}O_4$, m. p. 163—164° (corr.), obtained from 4-methylcarbonato-2-hydroxybenzoic acid by a modification of the preceding process, yields by hydrolysis *di-β-resorcylic acid*, $C_6H_3(OH)_2\cdot CO\cdot O\cdot C_6H_3(OH)\cdot CO_2H$, m. p. 215° (corr., decomp.).

3-*Methylcarbonato*-4-*hydroxybenzoic acid*, $CO_2Me\cdot O\cdot C_6H_3(OH)\cdot CO_2H$, m. p. 176° (corr., decomp.), obtained by the partial hydrolysis of the dimethylcarbonatobenzoic acid (Abstr., 1908, i, 892), is converted into *iso*vanillic acid by treatment with diazomethane and subsequent hydrolysis. When treated in acetone with *N*-sodium hydroxide and 3 : 4-dimethylcarbonatobenzoyl chloride in an atmosphere of hydrogen, it yields, after hydrolysis of the product, *diprotocatechuic acid*, $C_6H_3(OH)_2\cdot CO\cdot O\cdot C_6H_3(OH)\cdot CO_2H$, m. p. 237—239° (corr., decomp.).

Digallic acid, $C_{14}H_{10}O_9$, m. p. 282° (corr., decomp.), is obtained in a similar manner to the preceding acid; it precipitates solutions of albumin and of quinine acetate, and develops the usual bluish-black coloration with ferric chloride.

The following depsides have been prepared by similar methods. [With KURT HOESCH.]—*Diferulic acid*, m. p. 241—242°; *di*-o-*coumaric acid*, m. p. 188—190°; *di-β-hydroxynaphthoic acid*, m. p. 245°; 4-*feruloyloxybenzoic acid*, m. p. 233°; 4-*α-hydroxynaphthoyloxybenzoic acid*, m. p. 246—247°. [With R. LEPSIUS.]—*Disyringic acid*, m. p. 260°; *di*-m-*hydroxybenzoic acid*, m. p. 199°; 4-*syringoyloxybenzoic acid*, m. p. 208°; p-*hydroxybenzoylsyringic acid*, m. p. 282—284°; 4-m-*hydroxybenzoyloxybenzoic acid*, m. p. 239—240°; 3-p-*hydroxybenzoyloxybenzoic acid*, m. p. 254°. C. S.

p-Cresolglycuronic Acid. CARL NEUBERG and E. KRETSCHMER (*Biochem. Zeitsch.*, 1911, 36, 15—19).—Phenols excreted in the urine are never found in the free state, but as derivatives of glycuronic and sulphuric acids.

p-Cresol given to dogs was found to be excreted as a *p*-cresol derivative of glycuronic acid, $C_6H_9O_7\cdot O\cdot C_6H_4Me$, and as *p*-tolyl hydrogen sulphate.

A barium salt was isolated from the urine, which proved to be a mixed salt of these two acids. W. J. Y.

Cherry-laurel Water and Solutions of Benzaldehyde and Hydrocyanic Acid in Water. P. H. WIRTH (*Arch. Pharm.*, 1911, 249, 382—407).—An investigation of the equilibrium point reached

in aqueous solutions of benzaldehyde, benzaldehydecyanohydrin, and hydrogen cyanide under various conditions of temperature, concentration, acidity, alkalinity, etc., with special reference to the determination of the usual composition of cherry-laurel water (compare Denigès, Abstr., 1894, ii, 165; Fromm, Abstr., 1898, i, 266). The following points are established: All three compounds co-exist in aqueous solution, and the same equilibrium is reached whether the cyanohydrin or its two components be initially added to water. With increasing concentration, the equilibrium point moves in the cyanohydrin direction, and vice versa. The cyanohydrin is progressively dissociated into its components with rise of temperature. Alkalis in small quantities accelerate the rate at which equilibrium is reached, and cause dissociation of the cyanohydrin, but even in presence of considerable quantities of alkali the cyanohydrin is never completely dissociated (compare Ultée, Abstr., 1906, i, 5, and Rosenthaler, Abstr., 1909, i, 623). Equilibrium is reached less quickly in presence of acids. Silver nitrate produces silver cyanide in these solutions in presence of alkali, and the whole of the hydrogen cyanide may be thus removed, but in presence of acids the equilibrium is more stable, except under the influence of change of temperature or concentration.

The toxicity of benzaldehydecyanohydrin is proportional to the amount of hydrocyanic acid it can yield on dissociation. T. A. H.

Hydrogenation of Hydroaromatic Compounds. VICTOR SKWORZOW (*J. pr. Chem.*, 1911, [ii], 84, 422—424).—The usual methods of reduction when applied to hydroaromatic ketones either fail or give poor results. The author finds that the reduction may be effected quite easily, and with almost quantitative yield, by means of sodium and alcohol, if carried out under pressure in an autoclave. *l*-Menthone yields by this method a mixture of solid and liquid dextrorotatory menthols, whilst from *d*-pulegone a lævorotatory mixture was obtained. F. B.

Ketens. V. Reactivity of the Carbonyl Group. HERMANN STAUDINGER and N. KON (*Annalen*, 1911, 384, 38—135. Compare this vol., i, 462).—Previous experiments have shown that diphenylketen reacts with carbonyl compounds to form β-lactones or their products of decomposition, carbon dioxide and ethylene derivatives (Abstr., 1908, i, 410, 411; this vol., i, 459), and have demonstrated, although not conclusively, on account of complications introduced by side reactions, that the reactivity of the carbonyl group is strongly influenced by the neighbouring substituents (Abstr., 1910, i, 46). The present paper describes an exhaustive examination of this influence. The efficacy of the method of examination previously employed (Abstr., 1910, i, 46) has been tested by experiments with benzophenone or fluorenone; with these ketones side reactions are not possible. It is found that with molecular quantities, 1 : 1 or 1 : 10, of the ketone and diphenylketen (in the form of the solid diphenylketen-quinoline) at 131°, the expressions $x/at(a-x)$ or $1/t . \log a/(a-x)$ respectively are approximately constant during the first hour; subsequently their value diminishes, probably owing to the gradual polymerisation of the diphenylketen-

quinoline. (It has been found that extensive polymerisation of diphenylketen-quinoline occurs even at 131° in the presence of certain substances which catalytically accelerate the process. The polymeride does not react with carbonyl compounds.) Consequently, in the experiments with other carbonyl compounds, the amount of carbon dioxide evolved at the end of the first hour is taken as a measure of the reactivity of the carbonyl group, of course provided that the approximate constancy, during this interval, of one or other of the preceding expressions, according to the relative quantities of the carbonyl compound and diphenylketen employed, has afforded evidence that side-reactions have not occurred to an extent sufficient to nullify the results.

The influence of a number of like substituents on different carbonyl-containing groups has been examined in order to compare the reactivity of the carbonyl group in aldehydes, ketones, and acid derivatives. In the formula R·CO·R′, R is (I) Ph, (II) $OMe\cdot C_6H_4\cdot$, (III) $NMe_2\cdot C_6H_4\cdot$, (IV) CHPh:CH·, thus giving four series of carbonyl compounds. The figures in the following list give, for different R′'s, the percentage amount of the ketone which enters into the reaction during the first hour: R′=CHPh:CH, I. 31·4, II. 32·2, III. 52·3, IV. 69·0; R′=H, I. 3·8, II. 17·8, III. 53·0, IV. 38·3; R′=CN, I. 2·2, IV. 52·6; R′=Ph, I. 1·4, II. 4·2, III. 37·8, IV. 31·4; R′=Me, I. 2·2, II. 4·9, III. 11·4, IV. 16·3; R′=NMe_2, I. 2·5, II. 2·5, III. 12·2, IV. 11·4; R′=NPh_2, I. 2·5, IV. 4·8; R′=OMe, I. 0·2, II. 1·1, III. 4·0, IV. 1·3; R′=Cl, I. 0·2, II. 0·2, III. 1·6, IV. 4·0. Unfortunately, the results do not allow any definite conclusions to be drawn as to the influence of R and R′ on the activity of the carbonyl group, because the k of a unimolecular or bimolecular reaction is only approximately constant when R=Ph or $OMe\cdot C_6H_4$, and not at all constant in the other two series. However, several points are clearly indicated. Firstly, the reactivity of the carbonyl group is very differently influenced by different R′'s in the four series, but always in the same direction. Secondly, the reactivity of the carbonyl group is greatest in the neighbourhood of the styryl group and least in the acid chlorides and esters. Finally, compounds containing the cinnamoyl group are more reactive than those containing the benzoyl group.

The authors show that the varying reactivity of the carbonyl group cannot be explained by steric influences or by an increase or decrease in the basic character of the carbonyl group caused by the neighbouring groups, but attribute it to the varying degree of unsaturation of the carbonyl group; the greater the unsaturation of the group, the greater is its reactivity with diphenylketen. This leads them to a deduction which is emphasised throughout the paper. Since chromophores are unsaturated groups, the more unsaturated the carbonyl group the more chromophoric is its character. In their experiments the authors have observed that the carbonyl group in a coloured compound is more unsaturated (that is, more reactive) than that in a colourless compound of similar structure; moreover, influences which intensify the colour of a carbonyl compound also increase the unsaturation of the carbonyl group. A general review of these and of

previous experiments shows that quinones and unsaturated ketones react most energetically with diphenylketen, then come, in order of decreasing reactivity, aldehydes, aromatic ketones, and acid derivatives; it is the first two classes of compounds which are most prone to exhibit colour.

The reactivity of the carbonyl group in a series of compounds containing the cinnamoyl group cannot be compared by the amount of carbon dioxide evolved, because the reaction proceeds in two directions; thus diphenylketen and phenyl styryl ketone react:

$$\mathrm{CHPh{:}CH{\cdot}COPh + CPh_2{:}CO} \begin{cases} \longrightarrow \mathrm{CHPh{:}CH{\cdot}CPh{:}CPh_2 + CO_2} \\ \longrightarrow \mathrm{CHPh}<\begin{matrix}\mathrm{CH{:}CPh}\\ \mathrm{CPh_2{\cdot}CO}\end{matrix}>\mathrm{O} \end{cases}$$

(this δ-lactone was previously stated to be 3-benzoyl-1 : 1 : 2-triphenyl-4-*cyclo*butanone, Abstr., 1910, i, 46).

The great reactivity of the whole conjugated system in phenyl styryl ketone is very remarkable in contrast with the slight reactivity of benzaldehyde and of styrene with diphenylketen. In the conjugated system, $\underset{4}{\mathrm{C}}{:}\underset{3}{\mathrm{C}}{\cdot}\underset{2}{\mathrm{C}}{:}\underset{1}{\mathrm{O}}$, the addition of diphenylketen occurs the more in the position 1 : 4 the more the carbon atom 4 is rendered unsaturated by neighbouring substituents; addition in the position 1 : 2 predominates when the oxygen atom is rendered more unsaturated. In the "crossed" conjugate system, $\begin{matrix}\mathrm{C{:}C}\\ \underset{4}{\mathrm{C}}{:}\underset{3}{\mathrm{C}}\end{matrix}>\underset{2}{\mathrm{C}}{:}\underset{1}{\mathrm{O}}$, the distribution of the residual affinity is such that the oxygen is particularly unsaturated; consequently the addition of diphenylketen occurs very largely at the carbonyl group. For example, phenyl styryl ketone and diphenylketen react to the extent of 87% in the 1 : 2 position and 63% in the 1 : 4, whilst in the case of distyryl ketone the values are 71 and 29% respectively.

It is found, in general, that compounds containing a conjugated system are more reactive than those with a simple double linking, and that substances with a "crossed" system of double linkings are particularly unsaturated. Here again a parallelism is to be observed between unsaturation and colour; substances containing a conjugated system are more coloured than similar substances which do not, the colour being especially intense when a "crossed" conjugate system is present.

A similar parallelism is observed in the case of pyrone and *p*-benzoquinone; pyrones react very slightly with diphenylketen, whilst the quinones exhibit the greatest reactivity.

One of the most important points in the paper is the examination of the influence of auxochromic groups on the reactivity of a carbonyl group. (The auxochrome must be present as OR or $\mathrm{NR_2}$, since diphenylketen attacks the hydroxyl or amino-group in preference to the carbonyl group.) A study of the preceding list of compounds of the type R·CO·R′ shows that the methoxy-group, and particularly the dimethylamino-group, increases the reactivity of the carbonyl group;

their influence is greatest in the ortho-, and least in the meta-, position. Since it is well-known that auxochromes intensify colour, the parallelism between colour and unsaturation is manifested once again. The introduction of an acyl group into the hydroxyl or amino-group (which weakens the colour of the substance) causes a diminution in the reactivity of the carbonyl group.

Several other points, such as Kauffmann's inversion of chromophores and an explanation of the action of auxochromic groups, are discussed in the light of the theory that the reactivity of a group is dependent on its degree of unsaturation.

The following new compounds are described. The great majority of them have been obtained by the decomposition at 130—153° of the additive compound of diphenylketen and a carbonyl compound. p-*Methoxytriphenylethylene*, $OMe\cdot C_6H_4\cdot CH:CPh_2$, m. p. 81—82°, white crystals; p-*dimethylaminotriphenylethylene*, $NMe_2\cdot C_6H_4\cdot CH:CPh_2$, m. p. 126—127°, autoxidisable, yellow or yellowish-green crystals; *triphenyl*-p-*tolylethylene*, $CPh_2:CPh\cdot C_6H_4Me$, m. p. 153°; *diphenyldianisylethylene*, $CPh_2:C(C_6H_4\cdot OMe)_2$, m. p. 159—160°, colourless needles; p-*dimethylaminotetraphenylethylene*, $NMe_2\cdot C_6H_4\cdot CPh:CPh_2$, m. p. 173°; *tetramethyl*-pp′-*diaminotetraphenylethylene*,

$$CPh_2:C(C_6H_4\cdot NMe_2)_2,$$

m. p. 211—212°, yellowish-green crystals; *αε-tetramethyl*-pp′-*diaminodiphenyl-γ-diphenylmethylene-Δ^{αδ}-pentadiene*,

$$CPh_2:C(CH:CH\cdot C_6H_4\cdot NMe_2)_2,$$

m. p. 169—170°, yellowish-brown crystals; *benzhydrylidenebenzo*cyclo*heptadiene*, $C_6H_4<\begin{matrix}CH:CH\\CH:CH\end{matrix}>C:CPh_2$, m. p. 92°, yellow crystals; *benzhydrylidenedimethylbenzo*cyclo*heptadiene*,

$$C_6H_4<\begin{matrix}CH:CMe\\CH:CMe\end{matrix}>C:CPh_2,$$

m. p. 128·5—129°, colourless crystals; *benzhydrylidenediphenylbenzo*cyclo*heptadiene*, m. p. 181—182°.

p-*Dimethylaminoacetophenone*, m. p. 105·5°, is obtained in small yield by boiling dimethylaniline, acetic anhydride, and zinc chloride for four hours (the substance, m. p. 58°, described as *p*-dimethylaminoacetophenone in the literature is the monomethylated compound). *γ-Benzhydrylidenepentamethylene oxide*, $O<\begin{matrix}CH:CH\\CH:CH\end{matrix}>C:CPh_2$, m. p. 86°, unlike pyrone itself, possesses very weak basic properties. *Dimethylaminomethylenecamphor*, $C_8H_{14}<\begin{matrix}C:CH\cdot NMe_2\\ | \\CO\end{matrix}$, m. p. 63—64°, is prepared by treating a well-cooled, methyl-alcoholic solution of oxymethylenecamphor with the calculated amount of alcoholic dimethylamine.

C. S.

Stereoisomeric Chloroimino-ketones. PETER P. PETERSON (*Amer. Chem. J.*, 1911, 46, 325—344).—In a preliminary paper, Stieglitz and Peterson (Abstr., 1910, i, 323) have described the *α*- and *β*-chloroimides of *p*-chlorobenzophenone. A full account of the work is now given, together with a description of the *α*- and *β*-chloroimides of *p*-methoxybenzophenone and *pp*-chloromethoxybenzophenone.

Chloroiminobenzophenone, $CPh_2:NCl$, m. p. 37°, prepared by the action of hypochlorous acid on iminobenzophenone, forms yellow crystals.

*a-Chloroimino-*p*-methoxybenzophenone*, $OMe\cdot C_6H_4\cdot CPh:NCl$, m. p. 90°, crystallises in thin plates; the *β-compound*, m. p. 54°, forms large, asymmetric crystals. The two forms were proved to be structurally identical by treating them with dry hydrogen chloride, thus converting them both into chloroimino-*p*-methoxybenzophenone *hydrochloride*, which is decomposed by water into ammonium chloride and *p*-methoxybenzophenone.

p-*Chloro*-p-*methoxybenzophenone*, $C_6H_4Cl\cdot CO\cdot C_6H_4\cdot OMe$, m. p. 125°, was prepared by the action of anisole on *p*-chlorobenzoyl chloride in presence of aluminium chloride. *a-Chloroimino*-p-*chloro*-p-*methoxybenzophenone*, $ClC_6H_4.C(:NCl)\cdot C_6H_4\cdot OMe$, m. p. 94°, forms thin plates, and the *β*-compound, m. p. 65°, large crystals; their structural identity was proved in the same way as in the previous case.

o-*Chloro*-p-*methoxybenzophenone*, $C_6H_4Cl\cdot CO\cdot C_6H_4\cdot OMe$, obtained from *o*-chlorobenzoyl chloride and anisole, has b. p. 250°/50 mm.

E. G.

δ-Phenylbutyl Ketones and δ-Phenylvaleric Acid. WALTHER BORSCHE (*Ber.*, 1911, 44, 2594—2596).—The unsaturated condensation products of cinnamaldehyde and ketones obtained by the author (Abstr., 1910, i, 680) have been reduced by Paal's method with hydrogen and colloidal palladium to the corresponding saturated substances, thus yielding a series of ketones containing the group $CH_2Ph\cdot[CH_2]_3\cdot CO\cdot$, and therefore designated δ-phenylbutyl ketones. The simplest member, *δ-phenylbutyl methyl ketone*, $CH_2Ph\cdot[CH_2]_3\cdot COMe$, prepared from cinnamylideneacetone in cold methyl alcohol, is a highly refractive liquid, b. p. 268—269°, with a characteristic sweet odour; its *oxime* has b. p. 179—180°/12 mm. When shaken with a solution of bromine in 5% sodium hydroxide at 0°, the ketone yields bromoform, *δ-phenylvaleric acid*, m. p. 61°, in 35% yield, and the *methyl* ester, b. p. 173°/35 mm., of the acid.

C. S.

β-Keto-aa-dialkyl Alcohols. III. EDMOND E. BLAISE and I. HERMAN (*Ann. Chim. Phys.*, 1911, [viii], 23, 522—544. Compare Abstr., 1910, i, 534).—A continuation of the work described already (*loc. cit.*), the investigation being now extended to keto-alcohols containing a phenyl group.

*Phenyl acetoxy*tert.*-butyl ketone*, $OAc\cdot CH_2\cdot CMe_2\cdot COPh$, b. p. 155·5—156·5°/11 mm., prepared by the general method (Abstr., 1908, i, 248), furnishes a p-*nitrophenylhydrazone*, m. p. 125°, crystallising in long, orange-yellow needles from alcohol, and on hydrolysis by a cold 10% solution of potassium hydroxide in water yields *phenyl hydroxy*tert.*-butyl ketone*, b. p. 152—153°/12 mm. The latter furnishes an *oxime*, m. p. 122·5°, crystallising in slender needles, a p-*nitrophenylhydrazone*, m. p. 157°, forming yellow needles, and a *phenylurethane*, m. p. 89°, crystallising in long needles from benzene on addition of light petroleum. Both phenyl hydroxy*tert.*-butyl ketone and its acetyl derivative give on hydrolysis by warm alkalis phenyl *iso*propyl ketone

and formaldehyde. On dehydration by phosphoric oxide, phenyl hydroxy*tert.*-butyl ketone might be expected to yield tiglylbenzene or dimethylacrylbenzene, but the substance actually produced in this reaction appears to be *benzoylmethyl*cyclo*propane*, $COPh\cdot CMe<\begin{smallmatrix}CH_2\\|\\CH_2\end{smallmatrix}$, b. p. 117—119°. This gives a p-*nitrophenylhydrazone*, m. p. 175°, as a crystalline, yellow powder. *Tiglylbenzene* [*phenyl α-methylpropenyl ketone*], $COPh\cdot CMe\colon CHMe$, b. p. 117·5°/10 mm., obtained by condensing tiglyl chloride with zinc phenyl bromide, yields a p-*nitrophenylhydrazone*, m. p. 136°, crystallising in long, yellowish-red needles. *Dimethylacrylbenzene* [*phenyl* iso*butenyl ketone*],

$$COPh\cdot CH\colon CHMe_2,$$

b. p. 117°/10 mm., similarly prepared, gives a p-*nitrophenylhydrazone*, m. p. 132°, which crystallises from warm alcohol.

β-Acetoxy-β-phenylpivalyl chloride, $OAc\cdot CHPh\cdot CMe_2\cdot COCl$, b. p. 151°/9 mm., m. p. 41°, is readily converted into the corresponding p-*toluidide*, m. p. 191—192°. With zinc ethyl iodide, it condenses to form *ethyl β-acetoxy-β-phenyl*tert.*-butyl ketone*, $OAc\cdot CHPh\cdot CMe_2\cdot COEt$, b. p. 160—165°/11 mm., m. p. 42°, with some acetoxyphenylpivalyl anhydride and *iso*butenylbenzene (nitrosite, m. p. 154°). From the first of these products the corresponding keto-alcohol could not be prepared, since in contact with alkalis the acetoxy-compound readily decomposed into benzaldehyde and ethyl *iso*propyl ketone. As the keto-alcohol could not be isolated, its dehydration could not be studied. It should furnish *dimethylatropylethane*, $CMe_2\colon CPh\cdot COEt$, b. p. 124°/12 mm., which was prepared by condensing *dimethylatropyl chloride*, b. p. 120·5°/11 mm. (p-*toluidide*, m. p. 135—136°, slender needles), with zinc ethyl iodide. It furnishes a p-*nitrophenylhydrazone*, m. p. 129°, crystallising in yellowish-red needles from alcohol. T. A. H.

The Nature of the Carbon Double Linking. III. The Bromides of Anisylidenecinnamylideneacetone. HUGO BAUER and HEDWIG DIETERLE (*Ber.*, 1911, 44, 2691—2697).—Anisylidenecinnamylideneacetone (*p*-methoxystyryl β-styrylvinyl ketone),

$$CHPh\colon CH\cdot CH\colon CH\cdot CO\cdot CH\colon CH\cdot C_6H_4\cdot OMe,$$

may be prepared by condensing *p*-methoxystyryl methyl ketone with cinnamaldehyde by means of potassium hydroxide in alcoholic solution (compare Scholtz and Einhorn, Abstr., 1896, i, 368). When treated with bromine in glacial acetic acid solution, it yields a *dibromide*,

$$CHPh\colon CH\cdot CH\colon CH\cdot CO\cdot CHBr\cdot CHBr\cdot C_6H_4\cdot OMe,$$

and a *tetrabromide*,

$$CHPh\colon CH\cdot CHBr\cdot CHBr\cdot CO\cdot CHBr\cdot CHBr\cdot C_6H_4\cdot OMe,$$

crystallising in small, colourless needles, m. p. 139—140° and 155—156° respectively. The bromine atom adjacent to the anisyl group in these compounds is very mobile, and is readily replaced by alkyloxy-groups.

*ζ-Bromo-η-methoxy-α-phenyl-η-*p*-anisyl-Δ^{αγ}-heptadien-ε-one*,

$$CHPh\colon CH\cdot CH\colon CH\cdot CO\cdot CHBr\cdot CH(OMe)\cdot C_6H_4\cdot OMe,$$

prepared by boiling the dibromide with methyl alcohol, crystallises in light yellow plates, and gives a deep bluish-violet coloration with strong sulphuric acid; the corresponding *ethoxy*-compound is an oil.

ζ-Bromo-η-acetoxy-α-phenyl-η-p-anisyl-$\Delta^{\alpha\gamma}$-heptadien-ε-one,

$$CHPh\colon CH\cdot CH\colon CH\cdot CO\cdot CHBr\cdot CH(OAc)\cdot C_6H_4\cdot OMe,$$

obtained by the action of magnesium acetate on the dibromide in the alcoholic solution, crystallises in stout, pale yellow prisms, m. p. 78—79°.

γδζ-Tribromo-η-methoxy-α-phenyl-η-p-anisyl-Δ^{α}-hepten-ε-one,

$$CHPh\colon CH\cdot [CHBr]_2\cdot CO\cdot CHBr\cdot CH(OMe)\cdot C_6H_4\cdot OMe,$$

prepared either by boiling *p*-methoxystyryl β-styrylvinyl ketone tetrabromide with methyl alcohol or by the addition of bromine to the preceding bromomethoxy-compound in glacial acetic acid solution, crystallises in slender, white needles, m. p. 176—177·5°. When heated with pyridine, it loses hydrogen bromide, yielding *γζ-dibromo-η-methoxy-α-phenyl-η-p-anisyl-$\Delta^{\alpha\gamma}$-heptadien-ε-one,*

$$CHPh\colon CH\cdot CBr\colon CH\cdot CO\cdot CHBr\cdot CH(OMe)\cdot C_6H_4\cdot OMe,$$

which forms yellowish-brown leaflets, m. p. 174—175°.

That the addition of bromine to *p*-methoxystyryl β-styrylvinyl ketone takes place at the double linking adjacent to the anisyl group was proved by the oxidation of the above-mentioned ζ-bromo-η-methoxy-phenylanisylheptadienone by means of potassium permanganate in acetone solution to anisaldehyde and αβ-dihydroxy-γ-phenyl-γ-butyrolactone (Fischer and Stewart, Abstr., 1892, 1447). F. B.

Acylated Phenanthrenes and Some of their Derivatives. CONRAD WILLGERODT and BRUNO ALBERT (*J. pr. Chem.*, 1911, [ii], 84, 383—394).—9-*Acetylphenanthrene*, $C_{16}H_{12}O$, prepared by the interaction of acetyl chloride and phenanthrene in carbon disulphide solution in the presence of aluminium chloride, crystallises in leaflets, m. p. 123°, having a bluish fluorescence; it yields an *oxime*, crystallising in leaflets, m. p. 80°, and a *phenylhydrazone*, light yellow leaflets, m. p. 181°. When oxidised with five to six times its weight of chromium trioxide in glacial acetic acid solution, the ketone yields the ordinary form of phenanthraquinone, crystallising in needles, m. p. 205°. Oxidation with twice its weight of chromium trioxide results in the formation of a second modification, which crystallises in lustrous, golden leaflets, m. p. 204—205°, and is converted by dissolving in cold concentrated sulphuric acid or by prolonged heating with alcoholic potassium hydroxide into the ordinary form; the same transformation takes place when the leaflets are heated at 180—200°. Both forms yield with *o*-phenylenediamine the same phenanthraphenazine, m. p. 219—220°. When heated with yellow ammonium sulphide at 170—180°, acetylphenanthrene yields 9-*phenanthrylacetamide*, $C_{16}H_{13}ON$, crystallising in white leaflets, m. p. 250—252°, together with 9-*phenanthrylacetic acid*, $C_{14}H_9\cdot CH_2\cdot CO_2H$, which crystallises in small needles, m. p. 213—215°, and forms a yellow, gelatinous *silver* salt.

9-αα-*Dichloroethylphenanthrene*, $C_{14}H_9\cdot CMeCl_2$, prepared from 9-acetylphenanthrene and phosphorus pentachloride, crystallises in small, yellow needles, which decompose at 80—100° without melting.

Acetylphenanthrene is reduced by zinc and glacial acetic acid to 9-phenanthrylmethylcarbinol (Pschorr, Abstr., 1906, i, 820), and by hydriodic acid and phosphorus to 9-*ethylphenanthrene*, $C_{16}H_{14}$, which forms lustrous needles, m. p. 61°.

The interaction of phenanthrene and excess of acetyl chloride in the presence of aluminium chloride yields 9 : 10-*diacetylphenanthrene*, $C_{14}H_8(COMe)_2$, which crystallises in white needles, m. p. 178°, having a green fluorescence, and forms a *phenylhydrazone*, m. p. 189°, a *bisphenylhydrazone*, $C_{14}H_8(CMe{:}N{\cdot}NHPh)$, small, yellow needles, m. p. 238°, and a *dioxime*, leaflets, m. p. 258—260°. When oxidised with chromium trioxide in glacial acetic acid solution, the diacetyl derivative is converted into *phenanthrene*-9 : 10-*diketodicarboxylic anhydride*,

$$\begin{matrix} C_6H_4{\cdot}C{\cdot}CO{\cdot}CO \\ | \qquad \| \\ C_6H_4{\cdot}C{\cdot}CO{\cdot}CO \end{matrix}\!\!>\!O\,;$$

this forms a light yellow powder, m. p. above 360°, and yields a yellow *silver* salt, $C_{14}H_8(CO{\cdot}CO_2Ag)_2$.

By methods similar to those described in the case of the monoacetyl derivative, 9 : 10-diacetylphenanthrene has been converted into 9 : 10-*di-α-hydroxyethylphenanthrene*, $C_{14}H_8(CHMe{\cdot}OH)_2$, crystallising in leaflets, m. p. 165—166°, 9 : 10-*di-αα-dichloroethylphenanthrene*,

$$C_{14}H_8(CMeCl_2)_2,$$

which forms yellow leaflets, decomposing at 130—140° without melting, and 9 : 10-*diethylphenanthrene*, which crystallises in large, lustrous leaflets, m. p. 90—91°.

9-*Benzoylphenanthrene*, $C_{14}H_9{\cdot}COPh$, forms lustrous, white needles, m. p. 127°, and yields 9-*benzylphenanthrene*, crystallising in large, white leaflets, m. p. 91—92°, when distilled with zinc dust in a stream of hydrogen.

9 : 10-*Dibenzoylphenanthrene* forms leaflets, m. p. 317°; it is reduced by phosphorus and hydriodic acid at 180—190° to 9 : 10-*dibenzylphenanthrene*, which crystallises in needles, m. p. 180—182°. F. B.

The Two Forms of *o*-Benzoquinone. FRIEDRICH KEHRMANN (*Ber.*, 1911, **44**, 2632—2633).—The author is of opinion that the question, whether the two modifications of *o*-benzoquinone are isomeric and desmotropic, has not been answered; especially, a certain proof has not been given that the colourless form has the peroxide formula and the coloured form the diketo-formula. The colourless form has not been analysed, and might well be a hydrated *o*-benzoquinone, $O{:}C_6H_4{:}(OH)_2$, or even an additive compound containing ether (compare Willstätter and Müller, this vol., i, 728). C. S.

Action of Magnesium Methyl Iodide on *p*-Xyloquinone and Toluquinone. EUGEN BAMBERGER and LOUIS BLANGEY (*Annalen*, 1911, **384**, 272—322).—The action of magnesium methyl iodide on *p*-xyloquinone has been examined very thoroughly, and on toluquinone more superficially. In the former reaction the product obtained after the usual operations consists of unchanged material, amorphous substances, about 25% of *p*-xyloquinol, ψ-cumoquinol (1 : 2 : 5-trimethylquinol), ψ-cumenol, 2 : 2 : 5-*trimethyl*-2 : 3-*dihydro*-p-*benzoquinone*, $CO<\begin{matrix}CMe_2{\cdot}CH_2\\CH{=}CMe\end{matrix}>CO$, and smaller amounts of prehnitol, *tetramethyl*cyclo*hexandione*, and *di*-p-*xyloquinol monomethyl ether*, together with resinous and oily substances.

2 : 2 : 5-*Trimethyl*-2 : 3-*dihydro*-p-*benzoquinone*, [1 : 1 : 4-*trimethyl*-

Δ^3-cyclo*hexene*-2 : 5-*dione*] m. p. 86°, crystallises in large, highly refractive, yellow prisms, has an odour of camphor, is extremely volatile with steam, and forms a p-*nitrophenylhydrazone*, $C_{15}H_{17}O_3N_3$ (two forms, one having m. p. 244·5—245·5°, and the other decomposing at 306—308°), and a *bis-semicarbazone*, $C_{11}H_{18}O_2N_6$, blackening at 400°. *Tetramethyl*cyclo*hexandione*, which may have the constitution $CO<\begin{matrix}CH_2\cdot CMe_2\\ CMe_2\cdot CH_2\end{matrix}>CO$ or

$$CO<\begin{matrix}CHMe\cdot CHMe\\ CHMe\cdot CHMe\end{matrix}>CO$$

(the former being the more probable), forms colourless prisms, m. p. 110—111°, has an odour of borneol and peppermint, is extremely volatile with steam, and forms a *bis-semicarbazone*, $C_{12}H_{22}O_2N_6$, m. p. 330° (decomp.). *Di*-p-*xyloquinol monomethyl ether*,

$$CO<\begin{matrix}CH:CMe\\ CMe:CH\end{matrix}>C(OMe)\cdot C(OH)<\begin{matrix}CMe:CH\\ CH:CMe\end{matrix}>CO,$$

m. p. 220—220·5°, colourless needles, forms an *acetyl* derivative, $C_{19}H_{22}O_5$, m. p. 191—192°, p-*nitrophenylhydrazone*, $C_{23}H_{25}O_5N_3$, m. p. 272—272·5°, and a *semicarbazone*, $C_{18}H_{23}O_4N_3$, m. p. 272—273°.

3 : 4-Xyloquinol, toluhydroquinone, *p*-xylohydroquinone, and *p*-xyloquinol have been isolated from the product obtained from toluquinone and magnesium methyl iodide.

An examination of the constitutions of the preceding substances shows that in *p*-xyloquinone and toluquinone, which contain the system $\overset{1}{O}:\overset{2}{C}\cdot\overset{3}{C}:\overset{4}{C}\cdot\overset{5}{C}:\overset{6}{O}$, the addition of the magnesium methyl iodide occurs in the 1 : 2- or the 1 : 4-, but not in the 1 : 6-, position (compare Kohler, Abstr., 1905, i, 358). Consequently, the authors believe that during the reduction of quinones to hydroquinones the addition of the hydrogen does not take place directly at the oxygen atoms of the quinone, but in the 1 : 2- and 1 : 4-positions (above scheme), the hydroquinone being produced subsequently by intramolecular change.

C. S.

[Preparation of Anthraquinone Derivatives.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 234518).—When halogenated aromatic sulphones are boiled with α-aminoanthraquinones in a suitable solvent (such as nitrobenzene or naphthalene) in the presence of a condensing agent (copper acetate), compounds having valuable tinctorial properties are formed.

The *product* from α-aminoanthraquinone (1 mol.) and *pp*-dibromosulphobenzide forms brownish-red crystals, whilst the employment of 4-amino-1-benzylaminoanthraquinone and the foregoing sulphone furnishes a *compound*, violet crystals, which in the vat dyes wool a very fast violet colour.

The tinctorial properties of these and other compounds of a similar nature are tabulated in the original. F. M. G. M.

Preparation of Aminoanthraquinones and of Aminonaphthanthraquinones or their Derivatives. Badische Anilin- & Soda-Fabrik (D.R.-P. 234917).—Aminoanthraquinones and aminonaphthanthraquinones may be prepared by heating halogenated

benzoylbenzoic acids with ammonium hydroxide under pressure in the presence of a catalyst (such as copper), and submitting the amino-acids so obtained to the action of a dehydrating agent.

4(5)-*Chloro*-2-p-*toluoylbenzoic acid*, m. p. 168—170° (prepared from toluene and 4-chlorophthalic anhydride), was heated at 190—195° during twelve hours with 20% ammonium hydroxide in the presence of copper powder, the solution just acidified, and then neutralised with sodium acetate, when the *amino-acid* separated as a greyish-yellow powder.

2-*Amino*-6(7)-*methylanthraquinone*, orange-yellow needles, m. p. 256—257°, was obtained by heating the foregoing amino-acid at 200° with 10 parts of 90% sulphuric acid and subsequent crystallisation from xylene.

3(6)-*Chloro*-2-p-*toluoylbenzoic acid* (prepared from toluene and 3-chlorophthalic anhydride) yielded an *amino-acid* (pale grey powder), which was subsequently converted into 1-*amino*-6(7)-*methylanthraquinone*, red needles, m. p. 175°.

5′-*Chloro*-2-m-*xyloylbenzoic acid*, m. p. 162°, obtained from phthalic anhydride and *o*-chloro-*m*-xylene, gave an *amino-acid* crystallising in pale yellow needles, m. p. 140° (decomp.), and subsequently furnished 1-*amino*-2 : 4-*dimethylanthraquinone*, dark red crystals, m. p. 293°.

4(5)-*Chloro*-2-*naphthoylbenzoic acid*, m. p. 175° (prepared from naphthalene and 4-chlorophthalic anhydride), yielded a grey *amino-acid*, which was converted into an *aminonaphthanthraquinone*, glistening, red needles, m. p. 238°.

2′-*Chloro*-2-*naphthoylbenzoic acid*, m. p. 217—220°, obtained from phthalic anhydride and 2-chloronaphthalene, gave an *amino-acid* (a dark yellow powder), and finally an *aminonaphthanthraquinone*, brownish-violet, glistening needles, m. p. 182°. F. M. G. M.

Preparation of Condensation Products in the Anthracene Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 234977).—*Anthraquinone*-1 : 5-*bisanthranilic acid*, a dark violet powder, is prepared by heating potassium anthranilate in nitrobenzene solution with 1 : 5-dichloroanthraquinone in the presence of a condensing agent; when this is heated at 100° with concentrated sulphuric acid, it furnishes a condensation product in the form of a blue powder.

Anthraquinone-1 : 5-*bis*-o-*thiolbenzoic acid*, an orange-red powder, obtained in a similar manner from 1 : 5-dichloroanthraquinone and potassium *o*-thiolbenzoate in alcoholic solution, yields when heated at a higher temperature with sulphuric acid (23% anhydride) a product which forms a red powder. These compounds have probably the constitution : $C_6H_4{<}\genfrac{}{}{0pt}{}{X}{CO}{>}C_6H_2{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_2{<}\genfrac{}{}{0pt}{}{X}{CO}{>}C_6H_4$, where X is either sulphur or an imino-group. F. M. G. M.

Preparation of Anthraquinone Condensation Products. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 234922).—When 2-amino-anthraquinone is boiled (in nitrobenzene solution) with trichloro-

methyl mercaptan in the presence of a condensing reagent (such as copper), s-*dianthraquinonylthiocarbamide*,

$$CS\left(NH\cdot C_6H_3<^{CO}_{CO}>C_6H_4\right)_2,$$

is obtained in the form of a red powder.

The tinctorial properties of this and similar compounds obtained from 1 : 4-diaminoanthraquinone, $\alpha\beta$-diaminoanthraquinone, *p*-diaminoanthrarufin, 1-aminoanthraquinone, 1 : 4-aminohydroxyanthraquinone, and 1 : 5-diaminoanthraquinone respectively are tabulated in the original. F. M. G. M.

Chrysophanic Acid, Frangula-Emodin, and Some Oxonium Compounds of Anthracene Derivatives. OTTO FISCHER and HANS GROSS (*J. pr. Chem.*, 1911, [ii], 84, 369—382).—Chrysophanic acid may be obtained from chrysarobin by oxidation with chromic acid and demethylation of the resulting product by heating with hydrochloric acid in acetic acid solution. The mixture of chrysophanic acid and emodin thus obtained is separated by means of aqueous sodium carbonate. Successive treatment of the mixture with potassium hydroxide and methyl sulphate yields emodin trimethyl ether and chrysophanic acid dimethyl ether.

The transformation of diacetylchrysophanic acid into diacetylrhein is best accomplished by oxidation with chromic acid at 50—60° in a solution of equal parts of acetic anhydride and glacial acetic acid.

Dibenzoylchrysophanic acid, prepared by heating chrysophanic acid with benzoyl chloride in the presence of pyridine, crystallises in slender needles, m. p. 212° (compare de la Rue and Müller, this Journ., 1857, 10, 298). It is converted by oxidation with chromic acid into *dibenzoylrhein*, which crystallises in stellar aggregates of yellow prisms, m. p. 253—255°, and gives a red coloration with concentrated sulphuric acid.

When heated with concentrated ammonia, chrysophanic acid yields a *compound*, $C_{15}H_{11}O_3N$, crystallising in slender needles of a bronze lustre. The compound has the character of an amide, dissolves in alkalis and ammonia, forming reddish-violet solutions, and gives an orange coloration with sulphuric acid; the *ammonium* salt is unstable.

Triacetylemodin, prepared from frangula-emodin by heating with acetic anhydride and sodium acetate, has m. p. 196—197° (Liebermann gives 190°). It is oxidised by chromic acid to *triacetylemodic acid*, $C_{21}H_{14}O_{10}$, which crystallises in slender, yellow needles, and is hydrolysed by aqueous potassium hydroxide to *emodic acid*, $C_{15}H_8O_7$. The latter compound crystallises in orange-yellow needles, which decompose at 340—360°, and dissolve in alkalis with a reddish-violet coloration; it has the constitution of a trihydroxy-β-anthraquinonecarboxylic acid.

[With P. NEBER.]—A large number of anthracene derivatives have been studied with respect to their ability to form oxonium salts. Whilst anthracene and its methyl and chloro-derivatives together with anthraquinone, the methylanthraquinones, dimethyldihydroanthra-

quinone, and diethyldihydroanthraquinone do not yield oxonium salts with perchloric and hydrobromic acids, and the hydroxyanthraquinones give at most yellowish-red or red solutions, the alkyloxy-derivatives of anthraquinone often yield stable salts. From this the conclusion is drawn that the presence both of carbonyl and alkyloxy-groups is essential for the formation of stable oxonium salts in the anthracene series.

The following salts, all of which are red in colour, were isolated: the *hydrobromide*, $C_{18}H_{17}O_5Br$, the *zincibromide*, $C_{18}H_{17}O_5Br_3Zn$, and the *perchlorate*, $C_{18}H_{17}O_9Cl$, of emodin trimethyl ether; the *hydrobromide* and *zincibromide*, $C_{17}H_{15}O_4Br_3Zn$, of chrysophanic acid dimethyl ether, and the *hydrobromide* and *zincibromide* of dimethylchrysazin (1 : 8-dimethoxyanthraquinone). The hydrochlorides and zincichlorides may also be isolated, but these are more unstable than the corresponding bromides. The salts of 1 : 2-, 1 : 4-, 1 : 5-, and 1 : 6-dimethoxyanthraquinone and of rufigallol hexamethyl ether with perchloric or hydrobromic acid are too unstable to be isolated.

Rufigallol hexamethyl ether, $C_{20}H_{20}O_8$, prepared by the action of methyl sulphate on its potassium salt in the presence of anhydrous potassium carbonate, crystallises in light yellow needles, m. p. 240°.

F. B.

Relationship between Chrysophanic Acid, Aloe-Emodin, and Rhein. OTTO A. OESTERLE (*Arch. Pharm.*, 1911, **249**, 445—449).—It is now shown that on reduction aloe-emodin furnishes chrysophanhydranthrone, and this on oxidation by air in presence of sodium hydroxide solution furnishes chrysophanic acid. This observation in conjunction with those recorded already (Abstr., 1903, i, 356; 1908, i, 905; 1909, i, 946, and following abstract; Léger, Abstr., 1902, i, 549; Frobenius and Hepp, Abstr., 1907, i, 428; Robinson and Simonsen, Trans., 1909, **95**, 1085; Fischer, Falco, and Gross, Abstr., 1911, i, 309, and Tutin and Clewer, Trans., 1911, **99**, 946) indicates that rhein, aloe-emodin, and chrysophanic acid are 1 : 8-dihydroxyanthraquinones containing respectively a $-COOH$, $-CH_2OH$, and $-CH_3$ group in position 2.

T. A. H.

Constitution of Frangula-Emodin. OTTO A. OESTERLE and W. SYPKENS-TOXOPÉUS (*Arch. Pharm.*, 1911, **249**, 311—321).—The previous formulation of emodin as 3 : 6 : 7-trihydroxy-2-methylanthraquinone (Oesterle and Tisza, Abstr., 1908, i, 350) is of doubtful validity in view of Oesterle and Johann's observation (Abstr., 1910, i, 860) that methyl sulphate methylates both hydroxyl groups of chrysophanic acid, although one is probably in the α- and the other probably in the β-position. The results of investigations of the action of ethyl chloroacetate on emodin, and of aniline on tetranitro-emodin, indicate that two hydroxyls are in the α-position and one in the β-position, whence emodin is either 1 : 6 : 8-trihydroxy-2-methylanthraquinone or 1 : 5 : 7-trihydroxy-2-methylanthraquinone.

Emodin reacts with ethyl chloroacetate to form chiefly *ethyl*

emodinglycollate diacetate, $C_{14}H_4O_2Me(OAc)_2{\cdot}O{\cdot}CH_2{\cdot}CO_2Et$, m. p. 192—193°, which crystallises from alcohol on addition of chloroform, and when heated with potassium hydroxide in alcohol furnishes *potassium emodinglycollate*, crystallising in red needles. A small amount of *ethyl emodindiglycollate acetate*,

$$C_{14}H_4O_2Me(O{\cdot}CH_2{\cdot}CO_2Et)_2{\cdot}OAc,$$

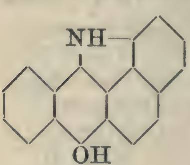
m. p. 152°, crystallising from 95% alcohol in bright yellow, slender needles, or from dry alcohol in thick needles, is formed. On hydrolysis this furnishes a *product*, m. p. 252—253° (decomp.), crystallising from pyridine on addition of alcohol.

Tetranitro-emodin, obtained by nitration of emodin with nitric acid (D 1·486—1·500), crystallises from acetic acid in orange-yellow needles and explodes when heated. When boiled with aniline during two hours, it furnished bluish-violet flocks of a *substance*, which agreed in ultimate composition with that required by the formula

$$C_{15}H_3O_2(NHPh)_3(NO_2)_2(NHPh)_2,$$

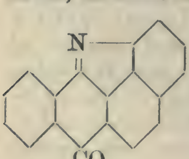
that is, tetranitro-emodin in which two nitro-groups have reacted with aniline and the three hydroxyl groups have been replaced by aniline residues (D.R.-P. 89080). This substitution of hydroxyl groups by aniline residues takes place most readily when the hydroxyl groups occupy para-positions with respect to nitro-groups in hydroxy-anthraquinones (*loc. cit.*) T. A. H.

Existence of Quinonoid Properties in Anthraquinone Derivatives. ROLAND SCHOLL [with G. VON WOLODKOWITSCH] (*Ber.*, 1911, 44, 2370—2377. Compare Bally and Scholl, this vol., i, 676).—1 : 2-Benzanthraquinone when nitrated with a mixture of nitric and acetic acids and acetic anhydride yields a mixture of two yellow mono-nitro-derivatives, $C_{18}H_9O_4N$, m. p. 277—278°, and 250—251°. On reduction of the less fusible isomeride with phenylhydrazine, the corresponding amine, $C_{18}H_{11}O_2N$, is not obtained, water being eliminated between the amino- and carbonyl group, and the anhydro-compound further reduced to *O,N*-dihydro-2 : 9-indoloanthrone (formula I), $C_{18}H_{11}ON$, a green substance. When dissolved in sodium hydroxide this compound is oxidised by the air to a brown substance, 2 : 9-indoloanthrone (formula II).



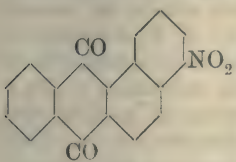
(I.)

This compound, in contrast to anthraquinone itself and its derivatives, exhibits marked quinonoid properties. It reacts energetically with phenylhydrazine, being reduced to the dihydro-compound (formula I above). It acts at the ordinary temperature in benzene or ethereal solution as an oxidising agent towards hydrogen iodide and sulphurous acid, colours hæmatoxylin red, but does not blue guaiacum resin. These pronounced quinonoid properties are considered to be due to the influence of the pyrrole nucleus attached to another nucleus of entirely different character, and so causing the existence of a carbon-nitrogen double bond of a highly unsaturated nature. This



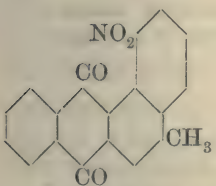
(II.)

influences the conversion of a neighbouring benzenoid linking into an ethenoid, and brings out the quinonoid properties of the anthraquinone.



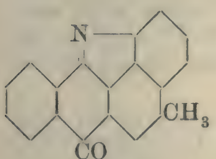
(III.)

The more fusible isomeric nitro-1 : 2-benzanthraquinone is converted on reduction into a red amino-1 : 2-benzanthraquinone, m. p. 215°, which, since it does not give a vat dye when fused with potassium hydroxide or heated with antimony pentachloride in nitrobenzene solution, is considered to have the amino-group in the benzene nucleus. The nitro-derivative accordingly has formula III.



(IV.)

3 - Methyl - 1 : 2 - benzanthraquinone when nitrated yields only one mononitro-derivative ; this must have the formula IV, since it is converted on reduction into a 3-methyl-2 : 9-indoloanthrone (V), which possesses typical quinonoid properties. An isomeric 4-nitro-derivative could not be obtained, owing to the steric hindrance of the methyl group occupying the a-position in the naphthalene nucleus.



(V.)

1-*Nitro*-1 : 2-*benzanthraquinone* forms yellow plates or prisms, m. p. 277—278°. The isomeric 4-*nitro*-1 : 2-*benzanthraquinone* crystallises in slender needles, m. p. 250—251°. Both isomerides dissolve in concentrated sulphuric acid with an orange-red coloration.

4-*Amino*-1 : 2-*benzanthraquinone* forms red crystals, m. p. 215°, and dissolves in concentrated sulphuric acid with a reddish-brown coloration.

O,N-*Dihydro*-2 : 9-*indoloanthrone* is a green powder, but forms brown or brownish-red solutions with a green fluorescence.

2 : 9-*Indoloanthrone* is obtained in violet-brown flakes, which sinter at 160°, but do not melt. E. F. A.

2 : 8- or *amphi*-Chrysoquinone. ERICH BESCHKE [with FRANZ DIEHM] (*Annalen*, 1911, **384**, 173—192. Compare this vol., i, 873).—2 : 8- or amphi-*Chrysoquinone*, $C_{18}H_{10}O_2$, m. p. 288—290° (decomp.), obtained by the action of lead dioxide on a suspension of 2 : 8-dihydroxychrysene in boiling acetic acid, crystallises in reddish-yellow needles, is odourless and non-volatile with steam, reacts instantly with phenylhydrazine or acidified potassium iodide, and forms a yellow, crystalline *compound*, $C_{18}H_{10}O_2,NaHSO_3,2H_2O$, with sodium hydrogen sulphite. Its suspension in hot alcohol reacts in the presence of atmospheric oxygen with dilute sodium hydroxide to form, after acidification, 8-*hydroxy*-1 : 2-*chrysoquinone*, $OH\cdot C_{18}H_9O_2$, dark red needles, decomp. above 300°, and with aniline or ethylaniline to form 8-*hydroxy*-1 : 2-*chrysoquinone*-1-*anil*, $OH\cdot C_{18}H_9O\colon NPh$, bluish-violet crystals, m. p. 230° (decomp. at 220°). The constitutions given to the two preceding substances are based on Willstätter and Parnas' experiences of the oxidising power of quinones of different types (Abstr., 1907, i, 1056), and are supported by the following evidence.

The chief proof is the fact that aniline or ethylaniline, reacting with 2 : 8-chrysoquinone, produce the same anil. 8-Hydroxy-1 : 2-chrysoquinone, which is also easily obtained by the action of sodium hydroxide and air on a boiling alcoholic suspension of 2 : 8-diacetoxychrysene, forms a *sodium* salt, $C_{18}H_9O_3Na$, bluish-violet, almost black needles, is reduced by sodium hyposulphite to the colourless 1 : 2 : 8-*trihydroxychrysene*, and forms an *acetyl* derivative, m. p. 252°, red needles, *ethyl ether*, m. p. 246°, and *benzoyl* derivative, m. p. 232°. It does not appreciably react at the ordinary temperature with phenylhydrazine, acidified potassium iodide, or sulphurous acid. A hot saturated solution of the quinone in glacial acetic acid reacts with concentrated alcoholic *o*-phenylenediamine to form 8-*hydroxy*-1 : 2-*chrysophenazine*, $OH\cdot C_{18}H_9<\!\!<^{N}_{N}\!\!>C_6H_4$, m. p. 292°, yellow needles, the *benzoyl* derivative, m. p. 270°, *acetyl* derivative, m. p. 252°, and *ethyl ether*, m. p. 215°, of which are respectively identical with the substituted chrysophenazines obtained by condensing *o*-phenylenediamine with the corresponding derivatives of 8-hydroxy-1 : 2-chrysoquinone.

8-Hydroxy-1 : 2-chrysoquinone-1-anil yields 8-hydroxy-1 : 2-chrysoquinone by hydrolysis with mineral acids, and yields with acetic anhydride an *acetyl* derivative, $C_{26}H_{17}O_3N$, m. p. 215°, which is converted by dilute hydrochloric and a little acetic acid into 8-acetoxy-1 : 2-chrysoquinone.

1 : 2 : 8-*Triacetoxychrysene*, $C_{18}H_9(OAc)_3$, colourless crystals, m. p. 195°, is obtained by treating a solution of 8-acetoxy-1 : 2-chrysoquinone in boiling acetic anhydride with zinc dust. 1 : 2 : 8-*Triethoxychrysene*, $C_{18}H_9(OEt)_3$, colourless crystals, m. p. 142°, is prepared by treating an aqueous alcoholic suspension of the sodium salt of 8-hydroxychrysoquinone, with dilute sodium hydroxide and sodium hyposulphite, and subsequently with ethyl sulphate. It has been found that 2-hydroxy-α-naphthaquinoneanil is produced when β-naphthaquinone is boiled with ethylaniline in alcoholic solution. C. S.

Condensation of Menthones with Organomagnesium Compounds. Synthesis of Homologues of Menthol. MARCEL MURAT (*J. Pharm. Chim.*, 1911, [viii], 4, 294—299).—Magnesium phenyl bromide reacts with menthone to give 1-3-*phenyl*-1-*methyl*-4-iso*propyl*-3-cyclo*hexanol*, $CH_2<^{CHMe\cdot CH_2}_{CH_2\cdot CHPr^{\beta}}>CPh\cdot OH$, b. p. 175°/20 mm., D^0 0·9962, n_D 1·527, $[\alpha]_D^{20}$ $-16·32°$. The *racemic* form prepared in the same way from thymomenthone had b. p. 170°/18 mm., D^0 0·9950. When treated with phenylcarbimide, or passed over alumina at 300°, dehydration occurs with production of the corresponding menthenes; 3-*phenyl*-1-*methyl*-4-iso*propyl*cyclo*hexene* has b. p. 268—272°/760 mm., D^0 0·9700, n_D 1·537. $[\alpha]_D$ $+13·9°$.

Magnesium *cyclo*hexyl bromide slowly acts on menthone, giving 3-cyclo*hexyl*-1-*methyl*-4-iso*propyl*-3-cyclo*hexanol*, monoclinic needles, m. p. 92°, together with 3-cyclo*hexyl*-1-*methyl*-4-iso*propyl*cyclo*hexene*, b. p. 265°/760 mm., D^0 0·9897, n_D 1·498, $[\alpha]_D$ $+6·2°$.

Thymomenthone (inactive menthone) was prepared by passing the vapour of Brunel's thymomenthol (Abstr., 1906, i, 81) over copper at

300°; it occurs as a viscid liquid, b. p. 212°, having a less pronounced odour than natural methone. When treated with magnesium *cyclo*hexyl bromide, it yields r-cyclo*hexylthymomenthol*, b. p. 164°/15 mm. (decomp.), D^0 0·9931, n_D^{17} 1·529; the corresponding cyclo*hexylthymomenthene* has b. p. 260°/756 mm. W. O. W.

Terpenes and Ethereal Oils. CVII. Constitution and Synthesis of Pinolone and of Dihydropinolone (3-Acetyl*iso*propyl*cyclo*pentane). OTTO WALLACH (*Annalen*, 1911, 384, 193—208).—Dihydropinolone, when prepared by the reduction of pinolone by Paal's method and purified through the *semicarbazone*, $C_{11}H_{21}ON_3$, m. p. 164—165°, is a colourless liquid with an odour of amyl acetate; it has b. p. 211°, D^{21} 0·8885, and n_D^{21} 1·4466. Its recognition as 3-acetyl*iso*propyl*cyclo*pentane, $CHAc<\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CHPr^\beta\end{matrix}$, has been accomplished by its degradation to *iso*propyl*cyclo*pentan-3-one, and by its synthesis from this substance. Its degradation is represented essentially by the scheme: dihydropinolone $\xrightarrow{NaOBr}$ $>CH\cdot CO_2H$ (b. p. 153—156°/16 mm.) $\longrightarrow$ $>CH\cdot CO\cdot NH_2$ (m. p. 164—165°; identical with Semmler's dihydrocamphoceenamide *b* [Abstr., 1906, i, 681]) $\xrightarrow[KOH]{Br\ and}$ $>CH\cdot NH_2$ $\longrightarrow$ $>CH\cdot OH$ $\xrightarrow{CrO_3}$ *iso*propyl*cyclo*pentan-3-one.

The synthesis has been accomplished as follows: The interaction of *iso*propyl*cyclo*pentan-3-one (prepared from tanacetophorone), zinc, and ethyl α-bromopropionate in benzene leads to the formation of an hydroxy-ester, which by successive boiling with acetic anhydride, hydrolysis by alcoholic potassium hydroxide, and acidification yields an acid, $CO_2H\cdot CMe\!:\!C<\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CHPr^\beta\end{matrix}$, the distillation of which in hydrogen produces a *hydrocarbon*, $C_{10}H_{18}$, b. p. 172—174°, D^{20} 0·809, n_D^{20} 1·4506. This hydrocarbon has assigned to it the constitution $CHMe\!:\!C<\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CHPr^\beta\end{matrix}$, on account of its exalted molecular refraction and its behaviour. It is practically identical with the *hydrocarbon*, $C_{10}H_{18}$, b. p. 171—174°, D^{22} 0·812, n_D 1·4515, obtained by heating *dihydropinolol*, $OH\cdot CHMe\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CHPr^\beta\end{matrix}$, b. p. 215—216°, D^{19} 0·8920, n_D 1·4569 (prepared by the reduction of dihydropinolone), with zinc chloride. The synthetic hydrocarbon (from the *iso*propyl*cyclo*pentanone) forms a blue *nitrosochloride*, which by successive treatment with boiling acetic acid and sodium acetate and with sulphuric acid is converted into a *ketone*, $COMe\cdot C<\begin{matrix}CH-CHPr_\beta\\ |\\ CH_2\cdot CH_2\end{matrix}$ (*semicarbazone*, m. p. 182—184°), isomeric with pinolone. This ketone yields dihydropinolone when reduced by Paal's method.

The series of transformations whereby pulegone dibromide is converted into pulegenic acid (Abstr., 1903, i, 567) has suggested an explanation of the course followed by pinyl tribromide during its

conversion into pinolone. This explanation leads to the conclusion that pinolone may be either

$$CMe_2{:}C{<}\begin{matrix}CH_2\cdot CH_2\\ \vert \\ CH_2\cdot CH\cdot COMe\end{matrix} \quad \text{or} \quad CH_2{:}CMe\cdot CH{<}\begin{matrix}CH_2\cdot CH_2\\ \vert \\ CH_2\cdot CH\cdot COMe\end{matrix}.$$

In harmony with this, the author finds that pinolonesemicarbazone, m. p. 158°, can be separated by repeated crystallisation into two portions, the less fusible of which has m. p. 173°. C. S.

Degradation of Nerol and its Constitution. A. BLUMANN and OTTO ZEITSCHEL (*Ber.*, 1911, **44**, 2590—2593).—When nerol or geraniol is oxidised by 1% potassium permanganate at 0° and the product is subsequently treated with dilute chromic and sulphuric acids, acetone, lævulic acid, and oxalic acid are obtained, the amount of lævulic acid being practically the same in each case. These results confirm the view that nerol and geraniol are stereoisomerides (Zeitschel, Abstr., 1906, i, 521). C. S.

Influence of Water on the Rotatory Power of Camphor Solutions. ENDRE VON KAZAY (*Pharm. Post*, 1911, **44**, 495—496).—The value of $[\alpha]_D$ for camphor in a number of organic solvents is about +43·6°, independent of the nature of the solvent. The addition of water to the alcoholic or acetic acid solution causes a very marked alteration in the rotation. When the proportion of water in the alcoholic solution containing about 12% of camphor is increased from 4% to 37%, the rotation diminishes from 8·3° to 7·1°. When in acetic acid solution containing about 10% of camphor, the proportion of water is gradually increased from zero to 32·3%, the rotation gradually diminishes from 8·3° to 6·0°. If the proportion of water in a solution is known, the percentage of camphor, p, can be calculated from the formula : $p=(100d)/(l[\alpha]_DB)$, where B is 0·1308 for acetic acid solutions, and 0·12822 for alcoholic solutions. G. S.

Effect of Molecular Symmetry on the Optical Activity and Relative Rotatory Power of Aromatic Position Isomerides. THOMAS P. HILDITCH (*Zeitsch. physikal. Chem.*, 1911, **77**, 482—497. Compare Trans., 1908, **93**, 1618 ; 1909, **95**, 1578).—A more detailed account of work already published (compare Proc., 1910, **26**, 141). The relative effects of ortho-, meta- and para-isomerides on the rotatory power is illustrated by the behaviour of compounds containing methyl, halogen, hydroxy-, methoxy-, nitro-, and amino-groups.

Sodium camphor-β-thiosulphonate, $C_{10}H_{15}O\cdot SO_2\cdot SNa$, is prepared by interaction of camphor-β-sulphonyl chloride and sodium sulphide in boiling alcohol. It occurs in soft, colourless, crystalline masses. The corresponding *acid* is an oily substance, and unstable. The *silver* salt forms a cream-coloured powder. The *anhydride*, $[(C_{10}H_{15}O)\cdot SO_2]_2S$, is obtained in almost theoretical yield by boiling equivalent amounts of the sulphonyl chloride and the sodium salt dissolved in carbon tetrachloride. It occurs in pale yellow needles, m. p. 144°.

Dicamphor-β-sulphonyl disulphide, $[(C_{10}H_{15}O)\cdot SO_2]S_2$, was obtained by the action of iodine, dissolved in potassium iodide solution, on

sodium camphor-β-thiosulphonate, and also by acting on the latter with sulphur monochloride in cold carbon tetrachloride. It occurs in colourless needles, m. p. 130°.

The phenyl camphor-β-sulphonates were all prepared by a modification of the Schotten-Baumann method. *Catechol dicamphor-β-sulphonate*, $C_6H_4(SO_3 \cdot C_{10}H_{15}O)_2$, forms colourless or slightly red crystals, m. p. 124°; the corresponding *resorcinol* compound melts at 129—130°, and the *quinol* compound at 187° (slight decomp.).

Pyrogallol tricamphor-β-sulphonate, $C_6H_3(SO_3 \cdot C_{10}H_{15}O_3)_3$, occurs in long, soft, colourless needles, m. p. 148° (decomp.). The corresponding *phloroglucinol* compound forms prismatic crystals, m. p. 104—106°.

G. S.

[Essential Oils.] SCHIMMEL & Co. (*Bericht*, October 1911, pp. 17—152).—*Artemisia biennis*, according to Rabak, yields 0·03% of a dark brownish-red, sweet-smelling oil, D^{25} 0·893, $[\alpha]_D$ +4·39°, n_D^{30} 1·5181, acid number 0, ester number 16, acetyl ester number 17·28, which dissolves in 4 vols. or more of 95% alcohol, and probably contains methylchavicole. According to the same author, *Artemisia serrata* yields 0·3% of a reddish-brown, bitter oil, D^{25} 0·913, α_D +6·8°, n_D^{30} 1·4602, acid number 1·6, ester number 10·0, acetyl ester number 43, which dissolves in 0·5 or more vols. 80% alcohol, and probably contains thujone.

Barosma crenulata (round buchu) leaves yield 1·7% oil, D_{15}^{20} 0·9364, α_D −15°22′, n_D^{20} 1·48005, which dissolves in 2·5 or more vols. of 70% alcohol with separation of paraffin, is brownish-yellow in colour after removal of traces of copper by acid, has mint-like odour, possibly due to menthone, and contains very little diosphenol.

Mandarin oil pressed from unripe fruits in Valencia had D^{15} 0·8665, n_D^{30} 1·47900, acid number 0·2, ester number 17·3, was incompletely soluble in 90% alcohol, and was of dark olive-green colour.

Helichrysum angustifolium oil from Dalmatia had D^{15} 0·9005, n_D^{20} 1·48209, acid number 0·9, ester number 61·1, and dissolved in 9 or more vols. of 90% alcohol. It was of olive-green colour, and resembled camomile oil in odour.

The Jalpaiguri (Indian) lemon-grass oils referred to previously (Abstr., 1910, i, 328) have now been found to be derived from *Cymbopogon pendulus*, Stapf.

Cayenne linaloe oil, like the Mexican product, contains methylheptenol.

Dalmatian laurel-leaf oil has D^{15} 0·9268, α_D −14°36′, n_D^{20} 1·46813, acid number 0·5, ester number 29·9, acetyl ester number 68·6, and is soluble in 2·5 or more vols. of 70% alcohol.

Dalmatian myrtle oil has D^{15} 0·9254, α_D +13°20′, n_D^{20} 1·46694, acid number 1·0, ester number 134·8, acetyl ester number 186·7, and is soluble in 3·2 or more vols. of 70% alcohol.

French peppermint, cultivated in Dalmatia, gave oils which after rectification had the following range of constants, D^{15} 0·9094—0·9141, α_D −11°45′ to −18°12′, n_D^{20} 1·46041—1·46783, acid number 0—1·0, total menthol 39·6—54·1%, ester menthol 2·6—3·8% and were soluble in 2·8 to 3 vols. of 70% alcohol with slight opalescence. According to

Henderson (*Chem. & Drug.*, 1911, **79**, 216), English peppermint grown on the banks of a river yielded only 0·1% oil, D 0·9046, a_D −27°, total menthol 59·2%, ester menthol 3·9%, whilst that grown in open fields on clay soil gave 0·409% oil, D 0·9065, a_D −27·4°, total menthol 61·35%, ester menthol 5·57%, and a third sample grown on sandy soil gave 0·19% oil, D 0·9046, a_D −28·2°, total menthol 59·46%, ester menthol 4·74%. Italian peppermint oil from Pancalieri had D^{15} 0·915, a_D −22°56′ to −26°51′, was soluble in 2·9 vols. of 70% alcohol, and deposited solid matter on cooling (Bourdet, *Bull. Sci. pharm.*, 1911, **18**, 372).

Sage oil distilled in Dalmatia in August from dry herb had the following normal constants, D^{15} 0·9165, a_D +25°, n_D^{20} 1·45871, acid number 1·0, ester number 9·3, whilst oil distilled from fresh herb in May had D^{15} 0·9111, a_D +20°22′, ester number 10·3, and was less soluble in alcohol than the August oil.

Origanum hirtum a-albiflorum herb grown in Dalmatia furnished origanum oil having the following range of constants, D^{15} 0·9231—0·94000, a_D +0°6′ to 0°20′, n_D^{20} 1·49394—1·50436, soluble in from 2·8 vols. of 70% alcohol to 1·5 vols. of 80% alcohol, and containing from 51 to 60% thymol.

Dalmatian spike oil had D^{15} 0·9022—0·9033, a_D −0°10′ to 0°53′, acid number 0·9, ester number 5·4—5·6, and was soluble in from 4 to 5 vols. of 60% alcohol. *Lavandula spica* herb from Spain yielded 1·9% of brownish-yellow oil, D^{15} 0·9100, a_D −2°20′, n_D^{20} 1·46823, acid number 3·7, ester number 7·0, and was soluble in 2 vols. of 70% alcohol, but became opalescent with more alcohol.

According to Jeancard and Satie (*Perf. and Essent. Oil Rec.*, 1911, **2**, 79) a so-called sandalwood from Guiana yielded oil having the following range of constants, D^{15} 0·963 to 1·0122, a_D +0°30′ to −6°, saponification value 13 to 65, after acetylation 65 to 117. On distillation it gave the following fractions: below 155°/20 mm., 18 to 27·4%, 155—160°/20 mm., 59 to 80%, and above 160°/20 mm., 2 to 13·6%. The second fraction contained a new constituent, *maroniol*, b. p. 158—159°/20 mm., D^{23} 1·0378, a_D −6°, which dissolved in 1·7 vols. 70% alcohol, and was colourless, viscous, and of agreeable odour; this substance is probably a tertiary alcohol.

Star anise oil contains *d*-*a*-pinene, *d*-*β*-phellandrene, dipentene, and *l*-limonene in the lower boiling fractions; as well as a fraction, 163—168°, having a turpentine-like odour, but which is free from *β*-pinene and sabinene.

Strobilanthes lupulinus flower buds yield an oil, D 0·9648, a −16°30′, n 1·4688, acid number 1·7, ester number 257 (*Perf. and Essent. Oil Rec.*, 1911, **2**, 96), having a strong, pleasant odour recalling those of tarragon and lavender.

A "wormwood" oil from Dalmatia had D^{15} 0·9188, acid number 1·3, ester number 64·4, and dissolved in 1 vol. 80% alcohol; it differed in odour from true wormwood oil, and was probably derived from another species of Artemisia. Wisconsin "wormwood" oil had D^{22} 0·9168, saponification number 150 (forty minutes), after acetylation 234·8 to 236·2, and was dark, with a mint-like odour. It contained much thujone, and on hydrolysis gave formic and salicylic acids.

Oil from *Gaultheria fragrantissima* of the Nilgiris, India, had D^{15} 1·1877, $\alpha_D \pm 0$, n_D^{20} 1·53485, ester number 364·8, was reddish-brown in colour and resembled winter green oil in odour.

Cananga oil from German East Africa distilled from fresh flowers had D^{15} 0·9366, $\alpha_D - 17°1'$, n_D^{20} 1·48451, acid number 1·1, ester number 136·3 and was soluble, with opalescence in 8 or more vols. of 80% alcohol.

Artemisia coerulescens herb from Turin gave 0·24% oil, D^{40} 0·9179, $\alpha_D - 5°50'$, acid number 11·3, ester number 42·0, which was brown and of buttery consistence, and had an odour recalling that of hyssop oil. The crystalline matter deposited by the oil melted at 108°.

Cardamom roots from Indo-China yielded 0·64% citron-yellow oil, D^{15} 0·9066, $\alpha_D - 32°57'$, n_D^{20} 1·48151, acid number 3·7, ester number 87·9, acetyl ester number 96·7, which was different from the seed oil in odour. It contained bisabolene, cineole, and paraffin.

Juniperus procera wood sawdust from German East Africa yielded 3·2% of oil, D^{15} 0·9876, n_D^{20} 1·50893, acid number 14·9, ester number 8·4, acetyl ester number 70. Fragments of the wood gave 3·2% of oil, which was semi-solid, and, after removal of solid matter, had D^{15} 1·0289, n_D^{20} 1·51011, acid number 27·06, ester number 7·93, acetyl ester number 89·6. The deposited crystals were cedar-camphor.

Cinnamomum Burmanni bark from Timor and the Celebes gave 0·5% oil, D^{15} 1·0198, $\alpha_D - 1°50'$, n_D^{20} 1·58282, which was not so pleasant n aroma as Ceylon cinnamon bark oil, but contained 77% of aldehydes and 11% phenols.

Meriandra benghalensis leaves from Erythraea gave 1·5% bright brown oil, D^{15} 0·9513, $\alpha_D - 2°5'$, n_D^{20} 1·47490, acid number 3·7, ester number 14·8, which had an odour resembling those of rosemary and sage. It deposited *d*-camphor when cooled.

Santolina chamaecyparissus herb from Turin gave 0·47% dark brown oil, D^{15} 0·9065, n_D^{20} 1·50040, acid number 6·6, ester number 16·4, acetyl ester number 74·2, with an odour resembling that of wormwood oil.

Satureja cuneifolia oils from Dalmatia had the following range of constants, D^{15} 0·9182 to 0·9440, $\alpha_D - 1°50'$ to 5°15', n_D^{20} 1·49816 to 1·50556, and contained from 28 to 59% of phenols, chiefly carvacrol, whilst the non-phenolic portion had a strong odour of cymene.

A résumé of literature published since April, 1911, on the analysis, physical properties, chemistry, etc., of essential oils and their constituents is also given. T. A. H.

[Essential Oils.] Roure-Bertrand Fils (*Sci. Ind. Bull.*, 1911, [iii], 2, 1—25).—[Justin Dupont and Louis Labaune.]—"Linalyl" bromide, obtained by esterifying either geraniol or linalool (Abstr., 1910, i, 184), condenses with ethyl sodiomalonate to form the *ester*, $C_{10}H_{17}\cdot CH(CO_2Et)_2$, b. p. 158—159°/5 mm., and this on hydrolysis gives the corresponding acid, $C_{10}H_{17}\cdot CH(CO_2H)_2$, which on distillation under reduced pressure furnishes the monobasic *acid*,

$$C_{10}H_{17}\cdot CH_2\cdot CO_2H,$$

b. p. 145—146°/5 mm., the *ethyl* ester of which has b. p. 127—128°/5 mm. The $\cdot C_{10}H_{17}$ group in the ester does not appear to have the geranyl configuration, since it is unaffected by sulphuric acid of 66° Bé. On reduction with sodium in alcohol, the ester yields a new *alcohol*,

$C_{10}H_{17}\cdot CH_2\cdot CH_2\cdot OH$, D^{18} 0·8956, n_D^{18} 1·4755, b. p. 119°/5 mm., which gives a crystalline *pyruvate*, b. p. 135°/6 mm., the *semicarbazone* of which crystallises from alcohol and melts at 103°. The alcohol is not converted into the corresponding alcohol by Sabatier and Senderens' method. All these substances possess weak and not very characteristic odours.

Linalyl bromide condenses similarly with ethyl sodioacetoacetate to form the *ester*, $C_{10}H_{17}\cdot CHAc\cdot CO_2Et$, b. p. 145°/6 mm., which on hydrolysis by potassium hydroxide in alcohol gives the *ketone*, $C_{10}H_{17}\cdot CH_2Ac$. The latter was not obtained pure, but it gives a *semicarbazone*, m. p. 86°, and on oxidation yields lævulic acid as chief product.

Ruta montana from Algeria furnishes an oil, D^{15} 0·8307, $\alpha_D + 0°42'$, soluble in 2·25 vols. 70% alcohol, which contains about 90% of methyl nonyl ketone. *Ruta bracteosa* from Algeria gives an oil, D^{15} 0·8410, $\alpha_D - 4°12'$, soluble in two vols. 70% alcohol, and containing 90% of ketones. This oil differs also from the foregoing in congealing partly at −5°, whilst the first oil is solid at +10°.

Inula viscosa oil from Algeria had D^{15} 0·9436 $\alpha_D - 24°0'$, and consisted chiefly of cineol.

Syrian origanum oil had D^{15} 0·9309 and $\alpha_D + 1°6'$, and was soluble in 1·2 or more vols. 80% alcohol; on standing it deposited a translucent "camphor." Syrian thyme oil, D^{15} 0·9120, $\alpha_D - 0°56'$, contained 43% phenols, composed of thymol and carvacrol. Syrian sage oil, D^{15} 0·9843, $\alpha_D - 6°8'$, was soluble in 1·5 or more vols. of 70% alcohol. Syrian laurel-leaf oil had D^{15} 0·9161 and $\alpha_D - 14°20'$, and was soluble in one or more vols. of 80% alcohol. Syrian neroli oil, D^{15} 0·8758, $\alpha_D + 1°6'$, saponification number 51·5, is similar to French neroli oil in constants. Syrian petit-grain oil had D^{15} 0·8857, α_D 3°24', saponification number 77·4, and was soluble in 1·25 or more vols. of 70% alcohol. T. A. H.

Essential Oil of Bupleurum fructicosum. II. LUIGI FRANCESCONI and G. SANNA (*Gazzetta*, 1911, 41, i, 796—813. Compare this vol., i, 658).—By fractional distillation of the essential oil of *Bupleurum fructicosum*, a large amount of a *terpene* is obtained as a mobile, colourless liquid, b. p. 167—169°, D^{14} 0·8416, $\alpha^{17} + 35·7°$, n_D 1·4862, which polymerises at 200°. The *polymeride* is a white, amorphous substance, m. p. 90—100° (becoming yellow), α^{14} −66·14° (in chloroform solution). The action of bromine on the terpene yields a colourless, viscous, non-crystalline substance, the amount of bromine absorbed indicating that the substance contains two double linkings. Hydrogen chloride also gives a non-crystalline product. With nitrosyl chloride, a small quantity of a *substance* was obtained, crystallising in small prisms, which begin to melt at 97°, and are entirely decomposed at 102°. When the residue from this reaction is distilled in steam, an *oil* is obtained, b. p. about 200° (partial resinification), which is dextrorotatory in alcoholic solution. The action of hydrazine and of phenylhydrazine does not yield crystalline compounds, but semicarbazide gives a *semicarbazone*, which forms silvery scales, m. p. 197—198°, and is dextrorotatory.

The essential oil also contains an *alcohol* and an *ether*. R. V. S

Extraction of an Aldehydic Perfume from Pine-wood Tar. FRIEDRICH MÜLLER (D.R.-P. 234794).—The fractional distillation of pine-wood tar furnishes at 150—200° substances of aldehydic nature and powerful odours, an *aldehyde* thus obtained formed a light brown oily liquid of high refractive index and characteristic odour; the crude distillate (b. p. 168—185°) after refractionation had b. p. 170—175° under atmospheric pressure, 75—85°/23 mm. and 51—56°/7 mm. with D^{17} 1·117. The *semicarbazone*, m. p. 184—186°, rhombic crystals; and an *oxime*, b. p. 170° (about) and D 0·8388 were also prepared. F. M. G. M.

Analysis of a Resin from an Egyptian Sarcophagus. REUTTER (*Compt. rend.*, 1911, **153**, 597—599).—The resin from a sarcophagus of the thirtieth dynasty has been shown to contain gum styrax from *Liquidambar orientalis*, Aleppo resin from *Pinus halepensis*, mastic from *Pistacia lenticus*, cedar wood oil, and asphalt. The ash contained sodium, calcium, aluminium, magnesium, traces of arsenic, chromium, iron, and manganese, carbonates, silicates, phosphates, chlorides, sulphates, and nitrates. The resin also contained sand, vegetable particles, and mineral fragments, of which an account is given.

W. O. W.

Constituents of Guayule, Parthenium argentatum. P. ALEXANDER (*Ber.*, 1911, **4**, 2320—2328).—This investigation was undertaken to ascertain, if possible, whether this plant, which is the source of guayule caoutchouc, contains any substance which can be regarded as the raw material from which caoutchouc is formed in plants. The results were negative from this point of view.

Guayule contains about 8—10% of caoutchouc, expressed on the dry material. The commercial caoutchouc from this source contains 75% of caoutchouc hydrocarbons, and does not differ from "hard Para rubber" to any greater extent than other second class rubbers. The dry plant yields about 6·5% of dark green, extractive matter to acetone, and of this 54%, 31%, and 15% are successively dissolved by light petroleum, ether, and hot alcohol, and of the three component parts thus separated, 12·1%, 7·0%, and 2·0% respectively consist of "unsaponifiable matter." The acids produced on hydrolysis of the extract include one melting at 119° and belonging to the cinnamic acid group, and phenylacetic acid. Weil states (Priv. com.) that he has found cinnamic acid in the products of hydrolysis of resin from guayule. The crude acetone extract on distillation with steam gives a *sesquiterpene alcohol*, m. p. 127—128°, with a camphoraceous odour.

On distillation with steam, guayule yields from 0·5 to 4% of volatile oil, D_{15}^{15} 0·8861, which is lævorotatory, possesses a peculiar pepper-like aroma, and consists almost wholly of hydrocarbons. On fractional distillation it gives 30%, b. p. 50—60°/17 mm.; 20·3%, b. p. 60—80°/17 mm.; 24·8%, b. p. 120—160°/17 mm., with 5% of resinous residue. The first fraction is mainly *l*-pinene, and the third fraction a *sesquiterpene*, D_{15}^{15} 0·9349, $[\alpha]_D^{16}$ − 21°24′, n_D^{16} 1·496. No styrene is present. The above relates to oil distilled from guayule in a fairly fresh state. Oil distilled from plants which had been stored several

years contained much oxygenated material, and although pinene was obtained from this oil no sesquiterpene fraction could be isolated. The presence of volatile oil in guayule is the cause of the difficulty at first experienced in the industrial use of caoutchouc from this source, since the oil hinders vulcanisation. T. A. H.

Cerebrosides of the Brain. HERMANN LOENING and HANS THIERFELDER (*Zeitsch. physiol. Chem.*, 1911, **74**, 282—289).—Methods are described for obtaining pure the galactoside known as cerebron (Thudichum's phrenosin). The presence of other galactosides of the nature of Thudichum's kerasin was also found. The work is to be carried further. W. D. H.

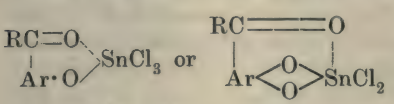
Saponins. RUDOLF KOBERT (*Chem. Zentr.*, 1911, 1, 1589; from *Unna Festschrift*, 1911, 1, 161—183).—Tables are given in the original of the chief members of the saponin series, $C_nH_{2n-8}O_{10}$, as well as of those of the digitonin series, $C_nH_{2n-16}O_{28}$, of the primary sapogenins (secondary glucosides), $C_nH_{2n-6}O_7$, and endsapogenins, $C_nH_{2n-6}O_2$, and also of sapogenins, $C_nH_{2n-6}O_3$. E. F. A.

Artemisinphenylhydrazone. PASQUALE BERTOLO (*Gazzetta*, 1911, **41**, i, 705—708. Compare Abstr., 1901, i, 718; 1908, i, 560).—*Artemisinphenylhydrazone*, $C_{15}H_{18}O_3$:N·NHPh, crystallises in yellowish-white, feathery needles, m. p. 144—145° (rapid heating), 221—222° (slow heating); $[\alpha]_D^{24}$ +180° (in alcohol). After the substance has been kept at 160° for a few minutes, the rotatory power is unchanged. The compound dissolves in concentrated sulphuric acid, giving a green coloration, which becomes cherry-red on addition of a trace of nitric acid. The phenylhydrazone differs from artemisin in that it is not acted on by alkalis. Prolonged reduction with sodium amalgam yields an acid *substance*. R. V. S.

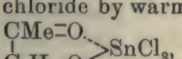
The Chlorophyll Group. The Duality of the Chlorophyllans and *allo*Chlorophyllan. LEON MARCHLEWSKI and J. MARSZAŁEK [with Z. LEYKO] (*Biochem. Zeitsch.*, 1911, **35**, 413—433).—Crude chlorophyll solutions from different sources, and even from the same plants, react in different ways when treated with zinc hydroxide and carbon dioxide. The chlorophyll from stinging nettles gives after treatment with these reagents for one day a fairly rapid change, but only a slight precipitate which has not the character of a zinc salt. In the chlorophyll, on the other hand, from maple leaves (*Acer pseudoplantanus*), only a small amount of the material enters into reaction with the zinc salt, and by such treatment the part which does not enter into combination can be separated from the other part. The "zinc chlorophyll" prepared from nettles contains more methoxyl and phytol when zinc acetate is employed for its preparation than when zinc hydroxide is used, and the latter exerts a slight hydrolytic action. The spectral measurements and extinction coefficients of this zinc derivative are given in some detail. Chlorophyllans were prepared from leaves of *Acer platanoides* from Poland and *A. pseudoplantanus* from Galicia, and analyses are given of the products obtained and also spectroscopic measurements. The analyses do not differ markedly from one another.

The spectroscopic measurements of the preparation from *A. platinoides* are intermediate between those obtained from nettles and maple. It is concluded that there is here a mixture of two chlorophyllans (chlorophyllan and *allo*chlorophyllan), and that certain varieties of plants are rich in the latter substance. By the separation of chlorophyllan by means of zinc hydroxide and carbon dioxide from *allo*-chlorophyllan (the method for which is given in detail) in a preparation rich in the latter and obtained from *A. platinoides*, a specimen of *allo*chlorophyllan was obtained of which the properties and spectroscopic measurements are given in some detail; this on saponification yields *allo*chlorophyllanic acids. These are reddish (and not olive-green) substances, from which fractions can be obtained by treating the ethereal solution with hydrochloric acid in various strengths. Only when 5% acid is used is any appreciable quantity of the pigment dissolved, and the basic character is therefore weak. By 7% acid a preparation of crystalline form was obtained. S. B. S.

Lakes. I. Paul Pfeiffer [with Z. Goldberg and J. Kuntner] (*Ber.*, 1911, **44**, 2653—2662).—The author hopes to bring Tschugaeff's (Abstr., 1907, i, 17, 392, 830) and Werner's (Abstr., 1908, i, 441) theories of the constitution of lakes into line with the theory by which he explains the phenomena of halochromy (Abstr., 1910, i, 852; this vol., i, 788). With this object in view, he has prepared, by heating the following *o*-hydroxy-ketones with tin tetrachloride (1·5 to 2 mols.) in dry benzene on the water-bath, coloured substances, which are represented by the annexed constitution. These substances are closely allied to the lakes of the tin series, which are obtained by replacing the chlorine atoms by hydroxyl groups.



The important question whether the tin is united co-ordinatively with the carbonyl oxygen atom is answered in the affirmative, not only because the author has already shown (*loc. cit.*) that carbonyl compounds of the most diverse character exhibit quite universally a tendency to unite co-ordinatively with tin tetrahalides, but also for the following reason. *m*- and *p*-Hydroxyacetophenone and tin tetrachloride in benzene, cold or hot, form normal additive compounds, $Cl_4Sn<\genfrac{}{}{0pt}{}{O{:}CMe\cdot C_6H_4\cdot OH}{O{:}CMe\cdot C_6H_4\cdot OH}$; *o*-hydroxyacetophenone and tin tetrachloride form in cold benzene a mixture of the normal additive compound and of the substituted compound, which evolves hydrogen chloride by warming, and changes entirely to the substituted *compound*,



, yellow crystals, m. p. about 238°.

In a similar manner, *o*-hydroxybenzophenone yields the similarly constituted *substance*, $C_6H_4Bz\cdot OSnCl_3$, pale yellow leaflets containing $\frac{1}{2}C_6H_6$, m. p. about 250° to a brown liquid; resacetophenone yields the *substance*, $OH\cdot C_6H_3Ac\cdot OSnCl_3$, pale yellow crystals, m. p. 235—248° to a red liquid (the additive *compound*,

$$2C_6H_3Ac(OH)_2,SnCl_4,$$

is precipitated first, and then changes to the substituted compound); quinacetophenone yields the *substance*, $OH\cdot C_6H_3Ac\cdot OSnCl_3$, deep yellow prisms; euxanthone yields the *substance*,

$$OH\cdot C_6H_3<\genfrac{}{}{0pt}{}{O}{CO}>C_6H_3\cdot OSnCl_3,$$

orange-yellow crystals; gallacetophenone yields the *substance*,

$$OH\cdot C_6H_2Ac<\genfrac{}{}{0pt}{}{O}{O}>SnCl_2,$$

deep yellow powder; and gallobenzophenone yields the *substance*, $OH\cdot C_6H_2Bz<\genfrac{}{}{0pt}{}{O}{O}>SnCl_2$, orange powder containing $\frac{1}{4}$—$\frac{1}{2}C_6H_6$. Of course, in all of these substances the tin is attached co-ordinatively to the carbonyl oxygen atom. C. S.

Aniline Black and its Intermediate Products. ARTHUR G. GREEN and SALOMON WOLFF (*Ber.*, 1911, **44**, 2570—2582).—In connexion with the series of quinonoid derivatives constituting the primary oxidation products of aniline, the various points of controversy between Green and Willstätter appear to turn on the claim of Willstätter and Dorogi (Abstr., 1909, i, 535, 975) that their triquinonoid black is identical with emeraldine [which is diquinonoid, according to Green and Woodhead (Trans., 1910, **97**, 2388)], but has the formula of Green and Woodhead's nigraniline; or, generally, the number of quinonoid nuclei in Willstätter's series of primary oxidation products of aniline is one greater than the number in Green's series. Willstätter and Cramer (this vol., i, 90) confirm Willstätter and Dorogi's views by estimating the number of quinonoid nuclei by means of phenylhydrazine at temperatures up to 150°. The authors now show that the phenylhydrazine process, although giving good results below 90°, is quite inaccurate at temperatures above 100°, owing to the spontaneous decomposition of the phenylhydrazine; emeraldine or nigraniline is completely reduced to the leuco-compound by phenylhydrazine at 80—90°, but when this temperature is exceeded a further evolution of nitrogen occurs without any further change in the reduced product.

In the preparation of their quinonoid blacks, Willstätter and Dorogi submit the product to a prolonged treatment with sulphuric acid. The authors condemn this process, since its effect is to convert triquinonoid and tetraquinonoid blacks into a mixture of emeraldine and polymerisation or decomposition products insoluble in 80% acetic acid. Dichromate black, prepared by Willstätter and Dorogi's method, omitting the acid treatment, is identical with Green and Woodhead's emeraldine; it dissolves completely in 80% acetic acid, forming a pale green solution, and yields by treatment with phenylhydrazine at 80—90° a volume of nitrogen corresponding with the diquinonoid formula. The preceding remarks serve to answer most of the recent criticisms of Willstätter and Cramer (this vol., i, 736). Their contention that Green and Woodhead's leucoemeraldine is not the real leuco-base, but is a monoquinonoid black, $C_{48}H_{40}N_8$, is regarded as extremely improbable. C. S.

Dimethylpyrone. ADOLF VON BAEYER and JEAN PICCARD (*Annalen*, 1911, **384**, 208—224).—2 : 4 : 6-*Trimethylpyroxonium perchlorate*, $CMe<\substack{CH\cdot CMe \\ CH:CMe}>O\cdot ClO_4$, colourless, indistinct prisms, m. p. 141—151° (decomp.), is obtained under the following definite conditions. A solution of dimethylpyrone in dry anisole at the ordinary temperature is cooled in a freezing mixture and treated with ethereal magnesium methyl iodide within the course of a minute. After one minute the mixture is added to 20% perchloric acid at −10°, and the perchlorate begins to crystallise almost immediately. 4-*Phenyl*-2 : 6-*dimethylpyroxonium perchlorate*, $C_{13}H_{13}O_5Cl$, sulphur-yellow leaflets, m. p. 210—212° (decomp.), is prepared in a similar manner; the *picrate*, $C_{19}H_{15}O_8N_3$, has m. p. 193°. All pyroxonium salts are converted into the corresponding pyridine compounds by aqueous ammonia in the cold; thus trimethylpyroxonium perchlorate yields 2 : 4 : 6-trimethylpyridine (*perchlorate*, m. p. 243—244°), the methiodide of which is converted by aqueous perchloric acid into 1 : 2 : 4 : 6-*tetramethylpyridinium perchlorate*, $C_9H_{14}O_4NCl$, m. p. 206—207°, which is also produced from trimethylpyroxonium perchlorate and methylamine. Trimethylpyroxonium perchlorate is converted by boiling alcoholic *p*-toluidine into 1-p-*tolyl*-2 : 4 : 6-*trimethylpyridinium perchlorate*, $CMe<\substack{CH\cdot CMe \\ CH:CMe}>N(C_7H_7)\cdot ClO_4$, m. p. 141—142°, whilst phenyldimethylpyroxonium perchlorate is converted similarly into 4-*phenyl*-1-p-*tolyl*-2 : 6-*dimethylpyridinium perchlorate*, m. p. 205°.

When an aqueous solution of trimethylpyroxonium perchlorate is boiled with barium carbonate in a current of hydrogen, δ-*methyl*-Δγ-*hepten*-βζ-*dione*, COMe·CH·CMe:CH·COMe, is obtained as an unstable oil, which has an odour of peppermint, regenerates the original perchlorate by warming with dilute perchloric acid, and forms a *disemicarbazone*, $C_{10}H_{18}O_2N_6$, m. p. 210—210·5°. δ-*Phenyl*-Δγ-*hepten*-βζ-*dione*, m. p. 51°, obtained in a similar manner from phenyldimethylpyroxonium perchlorate, is an unstable, colourless, crystalline powder. By reduction with palladium chloride and gum arabic in an atmosphere of hydrogen, it yields δ-*phenylheptane*-βζ-*dione*,

$$COMe\cdot CH\cdot CHPh\cdot CH_2\cdot COMe,$$

m. p. 61—62°. δ-*Methylheptane*-βζ-*dione*, b. p. 95—96°/12 mm., obtained in a similar manner, reacts very readily with semicarbazide, forming the *disemicarbazone*, $C_{10}H_{20}O_2N_6$, m. p. 199°. None of these δ-diketones give a reaction with ferric chloride. C. S.

β-Phenylcoumarins. I. GUIDO BARGELLINI and G. LEONARDI (*Gazzetta*, 1911, **41**, i, 737—746).—In the hope of obtaining compounds related to certain substances found in plants, the preparation of some hydroxyl derivatives of β-phenylcoumarin has been undertaken, using an old method for the preparation of coumarin derivatives (compare Komarovski and von Kostanecki, Abstr., 1894, i, 506).

2 : 3 : 4-Trihydroxybenzophenone, when heated for twenty hours with sodium acetate and acetic anhydride, yields the diacetyl-β-phenyldaphnetin of von Kostanecki and Weber (Abstr., 1894, i, 88).

2 : 4-Dihydroxy-4′-methoxybenzophenone (Komarovski and von

Kostanecki, *loc. cit.*) when heated for twenty hours with sodium acetate and acetic anhydride yields (1) a substance, probably the *diacetyl* derivative of 2 : 4-dihydroxy-4′-methoxybenzophenone ; and (2) an *acetyl* derivative of 4-*hydroxy*-4′-*methoxy*-β-*phenylcoumarin*, $C_{18}H_{14}O_5$, which forms colourless, woolly needles, m. p. 185—186°. By dissolving this substance in concentrated sulphuric acid and pouring the solution into water, 4-*hydroxy*-4′-*methoxy*-β-*phenylcoumarin*, $C_{16}H_{12}O_4$, is obtained ; it forms yellowish-white needles, m. p. 261—263°. The compound dissolves in alkalis, giving yellow solutions with a green fluorescence ; the solution in alcohol is also fluorescent, but the fluorescence disappears on the addition of acid. The substance dissolves in concentrated sulphuric acid, giving a green coloration. When it is treated with methyl iodide, 4 : 4′-*dimethoxy*-β-*phenylcoumarin*, $C_{17}H_{14}O_4$, m. p. 156°, is obtained.

2 : 4 : 4′-Trihydroxybenzophenone yields, when heated with sodium acetate and acetic anhydride, (1) *triacetoxybenzophenone*, which forms colourless needles, m. p. 96—98° ; (2) 4 : 4′-*diacetoxy*-β-*phenylcoumarin*, $C_{19}H_{14}O_6$, which crystallises in colourless needles, m. p. 189—190°. 4 : 4′-*Dihydroxy*-β-*phenylcoumarin*, $C_{15}H_{10}O_6$, prepared from it, forms yellowish-white needles, m. p. 238—240°. When treated with methyl iodide, it yields 4 : 4′-dimethoxy-β-phenylcoumarin, previously described. R. V. S.

β-Phenylcoumarins. II. Guido Bargellini and G. Forlì. Forti (*Gazzetta*, 1911, 41, i, 747—756. Compare preceding abstract) —The synthesis of β-phenylcoumarins has been continued by another method (compare von Kostanecki and Weber, Abstr., 1894, i, 88), namely, the condensation of *p*-cyanoacetylanisole or cyanoacetylveratrole (1 : 2-dimethoxy-4-cyanoacetophenone) with resorcinol or phloroglucinol.

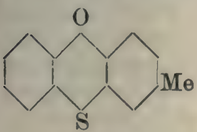
p-*Cyanoacetylanisole*, $C_{10}H_9O_2N$ (from *p*-chloroacetylanisole and potassium cyanide), crystallises in tufts of long, colourless needles, m. p. 128—130°. When it is heated with resorcinol and 73% sulphuric acid on the water-bath, two products are obtained : (1) a *substance*, soluble in water, which forms colourless needles, m. p. 234—236°, and is probably the nitrile or amide of the coumarin derivative, m. p. 260—262°, which it yields on addition of hydrochloric acid ; (2) 4-hydroxy-4′-methoxy-β-phenylcoumarin, m. p. 260—262°, identical with that described in the preceding abstract.

Condensation of *p*-cyanoacetylanisole with phloroglucinol yields a *substance*, m. p. about 200°, from which an *acetyl* derivative can be prepared, which crystallises in colourless needles, m. p. 179—180°.

Chloroacetylveratrole can be obtained : (1) by the action of methyl sulphate on chloroacetylcatechol ; and (2) by condensation of chloroacetyl chloride with veratrole in presence of aluminium chloride. In the second case another substance (? *chloroacetylguaiacol*) is the principal product ; in both cases the yield is exceedingly small. *Chloroacetylveratrole*, $C_{10}H_{11}O_3Cl$, crystallises in white scales, m. p. 102—104°. *Cyanoacetylveratrole*, $C_{11}H_{11}O_3N$, forms colourless needles, m. p. 134—135°. With resorcinol in presence of 73% sulphuric acid, it yields a *substance*, which crystallises in yellowish-

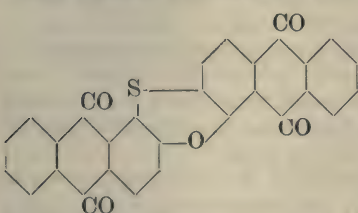
white needles, m. p. 228—229°, whilst with phloroglucinol a reddish-yellow condensation product is obtained. R. V. S.

Preparation of Phenothioxin and its Derivatives. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 234743).—It is found that the phenothioxin, m. p. 60—61°, b. p. 183—184°/12 mm., prepared by Mauthner (Abstr., 1906, i, 448) can be readily obtained by heating (with continual stirring) phenyl ether at 60—70° with sulphur in the presence of aluminium chloride; the temperature is subsequently slowly raised to 100° and maintained until evolution of hydrogen sulphide ceases. Under these conditions, *p*-tolylphenyl ether yields *3-methylphenothioxin* (annexed formula), m. p. 36°, b. p. 185—187°/12 mm., whilst *p*-chlorophenyl ether furnishes *3-chlorophenothioxin*, m. p. 37°, b. p. 176°/12 mm.



F. M. G. M.

[Preparation of Anthracene Derivatives.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 235094).—When anthraquinone-1-thiol is heated with 1-hydroxyanthraquinone at 160—170° in 98% sulphuric acid, it yields a *compound* (annexed formula), which crystallises from hot quinoline in brownish-red needles. The tinctorial properties of this and the following analogous condensation products are tabulated in the original.



1 : 5-Dithiolanthraquinone with 1- and 2-hydroxyanthraquinones (2 mols.) respectively; 1-thiolanthraquinone (2 mols.) and anthrarufin; 1-thiol-5-aminoanthraquinone and 5-amino-1-hydroxyanthraquinone; 1-thiolanthraquinone with 2-hydroxyanthraquinone; and 1-thiolanthraquinone (2 mols.) with anthraflavic acid; 2-thiolanthraquinone (1 mol.) with 2-hydroxyanthraquinone and (2 mols.) with anthraflavic acid. F. M. G. M.

Solubility of Alkaloids in an Aqueous Boric Acid-Glycerol Solution. E. BARONI and O. BORLINETTO (*Chem. Zentr.*, 1911, ii, 93—94; from *Giorn. Farm. Chim.*, 1911, 60, 193—195).—A solution containing 3·0 grams of boric acid, 50·0 grams of glycerol, and water to 100 c.c., dissolves the following quantities of various alkaloids, the figures in parentheses giving the solubility of the respective alkaloids in water: Codeine, 4% (1·66%); atropine, 10% (0·5%); cocaine, 8% (0·14%); morphine, 5·5% (0·1%); strychnine, 3·5% (0·01%); eserine, 7·5% (trace); veratrine, 6% (trace). The solubility of the alkaloids increases with the proportion of boric acid present in the solution. W. P. S.

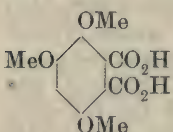
Crystalline Alkaloid of Calycanthus glaucus. IV. Some Salts of a New Quaternary Base obtained by Methylating *iso*-Calycanthine. HARRY M. GORDIN (*J. Amer. Chem. Soc.*, 1911, 33, 1626—1632).—When *iso*calycanthine (Abstr., 1910, i, 62) is treated

with methyl iodide, about 35% of the alkaloid is converted into the hydriodide, about 35% remains unchanged, and the remainder is converted into a quaternary iodide, $C_{24}H_{28}ON_3I,H_2O$. It is suggested that the oxygen of the air takes part in the reaction, as shown by the equations: $2C_{11}H_{14}N_2 + 2MeI + O_2 = C_{24}H_{28}ON_3I,H_2O + NH_4I$ and $C_{11}H_{14}N_2 + NH_4I = C_{11}H_{14}N_2,HI + NH_3$.

The quaternary *iodide* forms white, flat, lustrous needles, becomes brown at 213—214°, does not melt below 325°, and is soluble in about 30 parts of hot methyl alcohol; its *hydriodide* is described. The corresponding *chloride*, $C_{24}H_{28}ON_3Cl,3H_2O$, m. p. 220°, crystallises in flat, lustrous needles, and is soluble in about 50 parts of cold water; its *hydrochloride* is described. The *nitrate*, $C_{24}H_{28}ON_3\cdot NO_3$, m. p. 192—194°, forms white, rectangular prisms. The quaternary *picrate*, m. p. 155°, and *picrolonate*, m. p. 164—166°, are also described.

E. G.

Colchicine. I. and II. ADOLF WINDAUS (*Chem. Zentr.*, 1911, i, 1637—1638, 1638—1641; from *Sitzungsber. Heidelberger Akad. Wiss.*, 1910, 1—7; 1911, 1—27).—On oxidation of colchicine in 5% potassium hydroxide with potassium permanganate, in addition to oxalic acid, *trimethoxy-o-phthalic acid*, $C_{11}H_{12}O_7$, is obtained, which must have the annexed structure, since it differs from the trimethoxygallocarboxylic acid described by Feist.



By cautious sublimation of the reaction product in a vacuum at 220°, the *anhydride*, $C_{11}H_{10}O_6$, is obtained in needles, m. p. 143—144°. This is converted into the acid when boiled with water, which crystallises in transparent plates, m. p. 175—176°; the *silver* and *lead* salts are insoluble; the *barium* salt forms needles. The *anil* crystallises in colourless needles, m. p. 146°.

Derivatives of Trimethylcolchicinic Acid.—Colchicine was regarded by Zeisel as the methyl ester of an acid, colchiceine, but it is now considered to be an enolic methyl ether, colchiceine being an enol, since it gives a characteristic green coloration with ferric chloride. Zeisel has shown further, that colchiceine contains an acetyl group attached to nitrogen, so that the structure of colchicine may be expressed: $C_6H(OMe)_3{:}C_{10}H_8O(OMe)\cdot NH\cdot COMe$.

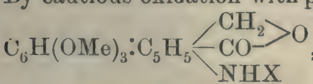
The almost colourless aqueous or alcoholic solutions of colchicine and its derivatives become deep yellow on the addition of hydrochloric acid, owing to the formation of acid additive products. *Trimethylcolchicinic acid dihydrochloride*, $C_{19}H_{21}O_5N,2HCl,H_2O$, forms dark yellow crystals; it still contains the free enolic group, and when heated at 100°, regenerates the monohydrochloride. *Trimethylcolchicinic acid dibenzoate*, $C_6H(OMe)_3{:}C_{10}H_8O(O\cdot COPh)\cdot NH\cdot COPh$, crystallises in faint yellow, three-sided prisms, m. p. 298° (decomp.); it gives no coloration with ferric chloride. N-*Benzoyltrimethylcolchicinic acid*, $C_6H(OMe)_3{:}C_{10}H_8O(OH)\cdot NH\cdot COPh$, prepared by heating the dibenzoate with 25% potassium hydroxide, separates in pale yellow needles, m. p. 253—254°, and gives a dark green ferric chloride coloration.

N-p-*Nitrobenzoyltrimethylcolchicinic acid* forms prisms, m. p. 256°. N-p-*Bromobenzoyltrimethylcolchicinic acid* separates in platelets, m. p. 253°. N-*Benzenesulphonyltrimethylcolchicinic acid*,

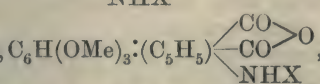
$$C_6H(OMe)_3{:}C_{10}H_8O(OH){\cdot}NH{\cdot}SO_2Ph,$$

forms greenish-yellow, rhombic plates, m. p. 255°, and gives an intense green ferric chloride reaction. *Trimethylcolchicinic acid dibenzenesulphonate*, prepared by the action of benzenesulphonyl chloride on the hydrochloride in pyridine solution, crystallises in yellow, four-sided, rhombic plates, m. p. 196°. The mother liquors contain an isomeric *dibenzenesulphonate*, crystallising in greenish-yellow prisms and plates, m. p. 141—142°. Neither isomeride gives any coloration with ferric chloride, and they are regarded as cis-, trans-isomerides.

Oxidation of Colchicine Derivatives with Potassium Permanganate.—By cautious oxidation with potassium permanganate, a lactone, *colchide*,

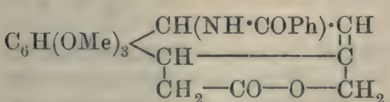


, and an acid anhydride, *colchinic anhydride*,

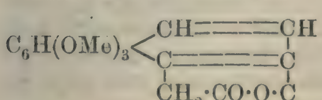


, have been obtained.

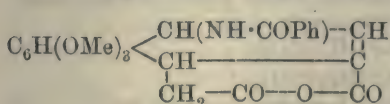
N-*Benzoylcolchide*, $C_{23}H_{23}O_6N$ (annexed formula), formed on oxidation of *N*-benzoyltrimethylcolchicinic acid, forms needles, m. p. 239°, $[\alpha]_D^{17}$ $-275°$; it gives no coloration with ferric chloride, and is neutral towards litmus paper.



On further oxidation trimethoxyphthalic acid is formed. It dissolves in alcoholic potassium hydroxide, the equilibrium between hydroxy-acid and lactone depending on the amount of alkali present. When heated for two hours at 250° under diminished pressure, benzamide and *trimethoxyhomonaphthide*, $C_{16}H_{16}O_5$, are obtained. The latter (annexed formula) crystallises in needles, m. p. 138°, is optically inactive, and behaves as a lactone; it is also formed on boiling *N*-benzoylcolchide with alcoholic hydrogen chloride, whereby, in part, benzoic acid and the corresponding amine, colchide, are formed; *colchide picrate*, $C_{16}H_{19}O_5N,C_6H_3O_7N_3$, crystallises in yellow prisms, m. p. 165°.



N-*Benzoylcolchinic anhydride* (annexed formula), prepared by oxidation of *N*-benzoyltrimethylcolchicinic acid, forms straggling, four-sided platelets, m. p. 207°, $[\alpha]_D^{18}$ $-288°$. The solutions in water and organic solvents are intense yellow, but the alkali salt solutions are colourless and remain so at first on the addition of acid; later they become yellow, and the anhydride crystallises. The *anil*, $C_{29}H_{26}O_6N_2$, forms almost colourless needles, m. p. 226°.



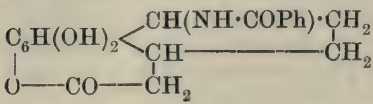
On heating with zinc dust and acetic acid, a tetrahydronaphthalene

derivative, $C_{23}H_{25}O_8N$, probably having the formula

$$C_6H(OMe)_3<\begin{array}{l}CH(NH\cdot COPh)\cdot CH_2\\ CH_2(CH_2\cdot CO_2H)\cdot CH\cdot CO_2H\end{array}$$

is obtained; it separates in colourless needles, m. p. 158° after previously sintering.

When the anhydride is warmed with hydriodic acid, the methyl groups and carbon dioxide are eliminated, and a compound, $C_{19}H_{17}O_5N$, having possibly the annexed formula is obtained; it crystallises in colourless needles, which darken at 200°, decomp. 230°.



The reasons for assigning the formula given to benzoylcolchinic anhydride are discussed at length.

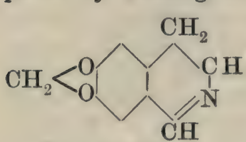
N-*Acetylcolchide* forms needles, m. p. 221°; the lactone ring is only opened with difficulty.

N-*Acetylcolchinic anhydride* forms deep yellow needles, m. p. 201°, and dissolves without colour in alkali hydroxides.

N-*Benzenesulphonylcolchinic anhydride*, $C_{28}H_{21}O_8NS$, crystallises in long, four-sided plates, m. p. 242—243° (decomp.). When hydrolysed and again acylated, it is converted into *N*-benzoylcolchinic anhydride.

E. F. A.

Preparation of Hydrastinine Salts. HERMAN DECKER (D.R.-P. 234850. Compare Abstr., 1908, i, 901).—When *formylhomopiperonylamine*, $CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot CH_2\cdot NH\cdot COH$, needles, m. p. 51—52° (prepared by heating homopiperonylamine formate at 160—170°), is heated with phosphoric oxide, it yields 6 : 7-*methylenedioxy*-3 : 4-*dihydroisoquinoline* (annexed formula), nodular crystals, m. p. 90—91°; its salts exhibit blue fluorescence, and the *picrate* has m. p. 238°; on treatment with methyl iodide, it furnishes hydrastinine hydriodide, and with methyl sulphate yields *hydrastinine methosulphate*, a yellow powder, m. p. 117—119°; the *picrate* has m. p. 175°.



F. M. G. M.

Action of Organic Magnesium Compounds on Hydrastinine. MARTIN FREUND and KARL LEDERER (*Ber.*, 1911, 44, 2356—2362). —Hydrastinine interacts with organo-magnesium compounds in a similar manner to cotarnine (Freund and Reitz, Abstr., 1906, i, 600), forming α-alkylhydrohydrastinine compounds of the type

$$CH_2O_2<\begin{array}{l}C{:}CH\cdot C\cdot CHR\cdot NMe\\ C{:}CH\cdot C\cdot CH_2-CH_2\end{array};$$

these are 1-alkyltetrahydro*iso*quinoline derivatives. Free hydrastinine gives a 50% yield; the hydrochloride reacts quantitatively with the Grignard reagent.

α-*Methylhydrohydrastinine* is an oil; the *hydriodide* crystallises in plates, m. p. 227°; the *methiodide* also forms plates, m. p. 229—230°.

α-*Ethylhydrohydrastinine* crystallises in hard, colourless plates, m. p. 70—71°.

α-*Phenylhydrohydrastinine* + H_2O forms long, pointed crystals, m. p. 88°; the anhydrous substance forms a yellow, resinous mass.

α-*Propylhydrohydrastinine* is oily; the *hydriodide* crystallises in plates, m. p. 185—186°; the *platinichloride* forms rhombic crystals, decomp. 230°; the *methiodide* separates in plates, which sinter at 163°, m. p. 168—169°.

iso*Propylhydrohydrastinine* is likewise oily. The *hydrobromide* crystallises in pointed needles, m. p. 190°; the *hydriodide* forms colourless, rhombic plates, m. p. 217—218°; the *picrate* forms plates, m. p. 143—145°; the *platinichloride* separates in needles, m. p. 223°; the *methiodide* forms bunches of needles, m. p. 219—220°.

α-*Butylhydrohydrastinine* is oily; it is characterised by the *picrate*, plates, m. p. 147—148°; the *platinichloride*, rhombic plates, m. p. 222—223°, and the *methiodide*, leaflets, m. p. 205—206°.

α-iso*Butylhydrohydrastinine* gives a *picrate*, crystallising in prisms, which sinter at 125°, m. p. 130°; a *platinichloride*, separating in four-sided plates, decomp. 220°, and a *methiodide*, which forms bunches of leaflets, m. p. 197—198°.

α-*Benzylhydrohydrastinine* is an oil, but forms crystalline salts. The *hydrochloride* forms six-sided crystals, m. p. 182°; the *hydrobromide* has m. p. 187—188°; the *hydriodide* crystallises in hexagonal plates, m. p. 195—196°; the *acid sulphate* sinters at 185°, m. p. 189°; the *picrate* forms octahedra, m. p. 178—180°; the *platinichloride* forms plates, decomp. 224°, whilst the *methiodide* forms aggregates of columnar crystals, m. p. 245°.

α-p-*Anisylhydrohydrastinine* crystallises in columns united in bundles, m. p. 98—99°; the *hydrochloride* forms needles; the *hydrobromide* is similar, m. p. 243—244°; also the *hydriodide*, m. p. 223—224°.

α-*Naphthylhydrohydrastinine* forms rhombic plates, which sinter at 125°, m. p. 127—128°. The *hydrochloride*, m. p. 254—255°; the *hydrobromide*, needles, m. p. 265°; the *hydriodide*, needles, m. p. 262°; the *acid sulphate*, matted crystals, which sinter at 225°, m. p. 228—229° (decomp.), and the *picrate*, plates, decomp. 201°, are described.

E. F. A.

Formation of Alkaloidal Periodides. W. C. Holmes (*Philippine J. Sci.*, 1911, *A*, 6, 253—275).—A résumé of the literature relating to the formation of alkaloidal periodides and the use of these compounds in the estimation of alkaloids is given. It is shown that morphine, codeine, and heroine, free or in the form of salts, have a remarkable affinity for iodine, and readily combine with it even in the absence of a solvent. There is no tendency to form definite compounds. The reactions are apparently dependent on the concentration of the iodine, and the phenomena observed are those of equilibrium involving vapour and osmotic pressures as factors. The amount of "free" iodine combined with the alkaloids cannot be determined by thiosulphate solution, and consequently it is considered that the formation and constitution of the periodides are much more complex than has been supposed.

When $N/10$-iodine solution is added to a 1% solution of codeine,

morphine, or heroine sulphate in $N/10$-sulphuric acid, and the uncombined iodine titrated wth $N/10$-sodium thiosulphate after standing overnight, the amounts of iodine absorbed by the alkaloids increase with the total concentration of iodine in the mixed solutions, but a maximum is soon reached in the case of heroine. When other factors are varied and the concentration of iodine and alkaloid kept constant, the amount of iodine absorbed varies inversely with rise in temperature, or increase in concentration of (*a*) sulphuric acid, (*b*) potassium iodide. Equilibrium appears to be reached in about thirty minutes. All the codeine precipitates were crystalline, as were also two of the morphine precipitates, whilst with heroine only amorphous deposits were obtained. The belief that in using Wagner's reagent for the estimation of alkaloids a definite amount of iodine combines with the alkaloid and may be determined by titration of the residual iodine is fallacious (compare Prescott and Gordin, Abstr., 1899, i, 89).

Aqueous solutions of free morphine, codeine, and heroine are precipitated by Wagner's reagent, and here, also, the amount of iodine absorbed is proportional to the concentration of iodine, and is inversely proportional to the amount of acid, which may be added subsequently. The free alkaloids and their sulphates also absorb iodine vapour when exposed to it, the salts being distinctly less active than the free bases.

T. A. H.

Methylation of the Alcoholic Hydroxyl Group in Morphine, Codeine, and the Methylmorphimethines. ROLAND PSCHORR and F. DICKHÄUSER [and, in part, C. D'AVIS] (*Ber.*, 1911, **44**, 2633—2640). —The alkylation of the alcoholic hydroxyl group in morphine, which has not hitherto been effected, proceeds quite easily in the cold when the alkaloid is shaken with methyl sulphate or methyl iodide and N-sodium hydroxide ($2\frac{1}{2}$ mols.). The product of the reaction, which is also obtained by starting with codeine, is precipitated by concentrated potassium iodide, whereby *methylcodeine methiodide*, decomp. 257° (corr.), $[\alpha]_D^{22}$ $-107{\cdot}2°$ in water, is obtained. A boiling aqueous solution of the methiodide is converted by 25% sodium hydroxide into *a-dimethylmorphimethine*, $C_{20}H_{25}O_3N$, leaflets or needles, m. p. 94°, $[\alpha]_D^{24}$ $-251{\cdot}9°$ in methyl alcohol (*methiodide*, $C_{21}H_{28}O_3NI$, decomp. 256° (corr.), $[\alpha]_D^{23}$ $-134{\cdot}4°$ in water), which is changed by heating with aqueous-alcoholic potassium hydroxide or with acetic anhydride at 210° to *β-dimethylmorphimethine*, isolated in the form of the *methiodide*, $C_{21}H_{28}O_3NI$, prismatic needles, decomp. 318—320° (corr.), $[\alpha]_D^{22}$ 268·5—278·5° in water.

The methylation of *a*- and *β*-methylmorphimethine is effected as in the case of morphine or codeine, the methiodides obtained being identical with those of *a*- and *β*-dimethylmorphimethine mentioned above. *γ-Dimethylmorphimethine methiodide*, $C_{21}H_{28}O_3NI$, leaflets, has decomp. 259° (corr.) and $[\alpha]_D^{20}$ $+14°$ in water. *δ-Dimethylmorphimethine methiodide*, needles, has decomp. 286° (corr.), and $[\alpha]_D^{28}$ 170·9° in water. *ε-Dimethylmorphimethine methiodide*, long needles, has decomp. 277° (corr.), and $[\alpha]_D^{20}$ $-79{\cdot}4°$ in methyl alcohol.

β-Dimethylmorphimethine methiodide is decomposed by aqueous-

alcoholic potassium hydroxide at 165°, forming morphenol, ethylene, and trimethylamine.

The methylation of various alcohols by sodium hydroxide and methyl sulphate has been examined. The method yields good results with benzyl alcohol and cinnamyl alcohol, but is unsatisfactory with *ter.*-amyl alcohol, octyl alcohol, borneol, and *iso*borneol. C. S.

Codeine Oxide. MARTIN FREUND and EDMUND SPEYER (*Ber.*, 1911, **44**, 2339—2353. Compare this vol., i, 76).—When codeine oxide, dissolved in acetic anhydride, reacts with sulphuric acid, two isomeric substances, $C_{18}H_{20}O_7NS$, are formed, both of which are acid in character, codeineoxidesulphonic acid (I.) and α-codeineoxidesulphonic acid (II.), these probably have the annexed constitutions; the α-compound is

$$\text{(I.)}\quad [C_{18}H_{20}O_3]\lessgtr\begin{matrix}SO_3H\\N\colon O\end{matrix}\qquad\qquad \text{(II.)}\quad [C_{18}H_{20}O_3]\lessgtr\begin{matrix}SO_2\\N(OH)\end{matrix}\!\!>O$$

easily converted into the isomeride.

On reduction, both are converted into the same codeinesulphonic acid, $N⋮[C_{18}H_{20}O_3]\cdot SO_3H$. This, on treatment with nitric acid, yields the nitrocodeine described by Anderson. Proof that no change in the structure of the alkaloid complex has taken place is afforded by the fact that all the sulphonic acids described yield codeine when superheated with water. When dissolved in cold concentrated sulphuric acid, the sulphonic acids, however, are more profoundly altered, and new products are obtained which await further investigation.

Codeinesulphonic acid when treated with methyl iodide in alkaline solution forms codeinesulphonic acid methyl hydroxide,

$$NMe\colon[C_{18}H_{20}O_3](OH)\cdot SO_3H.$$

On boiling with alkali, βγ-dimethylbutylene-βγ-diamine is eliminated and a nitrogen-free product obtained, which could not be isolated. After remaining in alkaline solution with methyl iodide and alcohol for some time and then boiling, the methyl hydroxide is converted into a crystalline salt, $C_{16}H_{11}O_6SK$, which is regarded as a morphenol derivative, $O\colon C_{14}H_5(OMe)_2\cdot SO_3K$.

α-Codeineoxidesulphonic acid behaves in many respects otherwise than the isomeride. With nitric acid a nitro-compound,

$$O\colon N⋮[C_{18}H_{19}O_3](NO_2)\cdot SO_3H,$$

is obtained. Sulphurous acid converts this into a nitrocodeine isomeric with Anderson's, but both isomerides give the same aminocodeine when reduced.

When α-codeineoxidesulphonic acid is treated with bromine water, and the perbromide formed is boiled with alcohol, a compound, $C_{15}H_{17}O_4Br_3$ or $C_{15}H_{15}O_4Br_3$, is obtained of unknown constitution.

Morphine oxide, when similarly treated with acetic anhydride and sulphuric acid, forms a bimolecular hydroxysulphonic acid, $C_{34}H_{40}O_{15}N_2S_2$, which is converted by sulphurous acid into a compound, $C_{17}H_{21}O_7NS$.

Codeineoxidesulphonic acid forms small crystals of the hexagonal system, decomp. 272°, $[\alpha]_D$ −115·4°, and forms a crystalline *potassium* salt.

Codeinesulphonic acid is dimorphous, crystallising in well-formed prisms and silky needles, which can be converted into one another. It decomposes above 300° and has $[\alpha]_D$ −136·3°.

Codeinesulphonic acid methylhydroxide separates in needles, decomp. 284°, $[\alpha]_D$ $-63{\cdot}2°$. Treatment with methyl iodide and alcohol and subsequent boiling with alkali gives a *compound*, $C_{16}H_{11}O_6SK$, crystallising in well-formed plates, decomp. 295°. On treatment of codeineoxidesulphonic acid with cold concentrated sulphuric acid, a substance, $C_{18}H_{21}O_6NS$, provisionally termed *β-codeinesulphonic acid*, is obtained. It forms bundles of microscopic plates, decomp. 243°, $[\alpha]_D$ $-190{\cdot}1°$. Sulphurous acid converts this into an isomeric substance, provisionally termed *γ-codeinesulphonic acid*, which crystallises in matted needles, decomp. 280°.

Potassium chromate oxidises codeineoxidesulphonic acid into *codeineoxidesulphonic acid hydrate*, $C_{18}H_{23}O_8NS$, crystallising in needles; on heating at 180° with water under pressure, a *base* separating in stunted, prismatic plates or long needles, m. p. 180°, is obtained; the *hydrochloride* forms long needles, m. p. 310°.

Concentrated sulphuric acid converts codeinesulphonic acid into a *compound*, $C_{19}H_{18}O_3N{\cdot}SO_3H$, which crystallises in very slender needles, decomp. 285—290°.

a-Codeineoxidesulphonic acid crystallises in stunted prisms; it is converted into the isomeride on heating with 10% sodium hydroxide or 20% hydrochloric acid.

Nitro-a-codeineoxidesulphonic acid crystallises in yellow plates, decomp. 167—170°.

a-Nitrocodeine, prepared by the action of sulphurous acid on the sulphonic acid, crystallises in microscopic, four-sided plates, m. p. 197°.

By the interaction of bromine and a-codeineoxidesulphonic acid, a *compound*, $C_{15}H_{17}O_4Br_3$, is obtained in long needles, m. p. 258—260° (decomp.).

Codeinesulphonic acid is without physiological action.

Both the isomeric nitrocodeines when reduced electrolytically yield the same *aminocodeine*, $C_{18}H_{20}O_3N{\cdot}NH_2$, crystallising in plates, m. p. 228°. The *hydrochloride* forms needles, m. p. 290°.

Hydroxycodeine, prepared by diazotisation of aminocodeine and boiling, crystallises in colourless plates, which when heated lose water at 176—185°, m. p. 234°. The *hydrochloride* crystallises in needles.

E. F. A.

Cotarnine. VI. Martin Freund and Karl Lederer (*Ber.*, 1911, **44**, 2353—2356).—Tarconine methiodide reacts with magnesium phenyl iodide, forming 8-*methoxy*-6 : 7-*methylenedioxy*-1-*phenyl*-2-*methyl*-1 : 2-*dihydroiso*quinoline, $CH_2<\begin{matrix}O{\cdot}C{:}C(OMe){\cdot}C{\cdot}CHPh{\cdot}NMe \\ O{\cdot}C{:}CH\text{——}C{\cdot}CH=CH\end{matrix}$. On reduction this is converted into a-phenylhydrocotarnine (8-methoxy-6 : 7-methylenedioxy-1-phenyl-2-methyltetrahydro*iso*quinoline), previously prepared by Freund and Reitz (Abstr., 1906, i, 600) from cotarnine salts and magnesium phenyl iodide.

a-Phenyltarconine forms colourless bunches of pointed crystals, which sinter at 97°, m. p. 102°. The salts and methiodide are oily, and decompose with a red coloration.

a-Butylhydrocotarnine, $CH_2O_2<\begin{matrix}C{:}C(OMe){\cdot}C{\cdot}CH(C_4H_9){\cdot}NMe \\ C{:}CH\text{——}C{\cdot}CH_2\text{——}CH_2\end{matrix}$, pre-

pared from cotarnine hydrochloride and magnesium butyl bromide is an oil. The following crystalline salts have been analysed: *hydrochloride*, plates, m. p. 215—216°; *hydrobromide*, plates, m. p. 207—208°; *hydriodide*, columns, m. p. 190—191°; *picrate*, plates, m. p. 165—166°; *platinichloride*, plates, m. p. 205—206°; *methiodide*, long, rhombic plates, m. p. 190—193°. E. F. A.

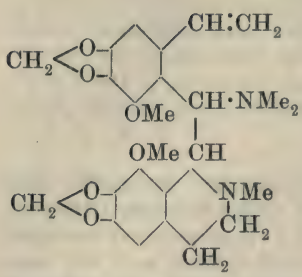
Stereochemistry of Nitrogen Compounds. Isomeric Bis-hydrocotarnines. MARTIN FREUND and OTTO KUPFER (*Annalen*, 1911, **384**, 1—38).—Bis-hydrocotarnine (di-hydrocotarnine) has been prepared by Freund and Reitz (Abstr., 1906, i, 600), and the constitution ascribed to it by these authors has been confirmed by Freund and Lederer (see Lederer, *Diss.*, Giessen, 1909) and yet again by the present authors, who have oxidised the substance to cotarnine nearly quantitatively by dilute sulphuric acid and 10% potassium dichromate. From its constitution (the molecule consists of two structurally identical halves, each containing an asymmetric carbon atom) it is obvious that a stereoisomeride should exist, and, indeed, a repetition of Freund and Reitz's experiment has shown that, in addition to the bis-hydrocotarnine already isolated, a small quantity of the isomeride, iso-*bishydrocotarnine*, $C_{24}H_{28}O_6N_2$, is formed. The two compounds have the same m. p., 163—164° (when mixed m. p. about 20° lower), but show marked dissimilarities in the solubilities of their salts; they are easily separated almost quantitatively by means of their *hydrogen sulphates*, that of bishydrocotarnine being very sparingly soluble in dilute sulphuric acid. Bishydrocotarnine forms a dihydrochloride, m. p. 231—232°, dihydrobromide, decomp. 228—229°, dihydriodide, m. p. 228—230°, *dihydrofluoride*, m. p. 227—229°, and *dinitrate*, m. p. 169—171°, whilst *iso*-bishydrocotarnine forms corresponding salts having the same m. p. (the mixed m. p. is always lower). It is changed to bishydrocotarnine at 160°, and gives a quantitative yield of cotarnine by oxidation with potassium dichromate and sulphuric acid.

Possibly bishydrocotarnine and *iso*bishydrocotarnine represent racemic and meso-modifications. However, all attempts to resolve either of them having been unsuccessful, this problem has been put aside for the present, although the suggestion is advanced that the two substances may be cis- and trans-modifications of the meso-form, as in the case of coniine and *iso*-coniine. *iso*-Bishydrocotarnine forms a *methiodide*, $C_{24}H_{28}O_6N_2,MeI$, m. p. 233°. The fact that bishydrocotarnine forms only a monomethiodide (*loc. cit.*) is due to steric hindrance, because when the methiodide is converted into the corresponding *hydroxide*, $C_{24}H_{28}O_6N_2,MeOH,10H_2O$, m. p. 75—80°, and this is treated with methyl iodide, the *methiodide*,

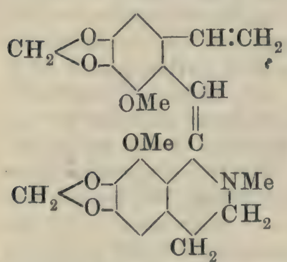
$$C_{24}H_{28}O_6N_2,MeOH,MeI,$$

m. p. 215—216°, is obtained, which is converted by acetic acid and potassium iodide into *bishydrocotarnine dimethiodide* $C_{24}H_{28}O_6N_2,2MeI$, m. p. 201—202°.

When treated with silver oxide and water and subsequently boiled with concentrated potassium hydroxide, bishydrocotarnine methiodide and *iso*-bishydrocotarnine methiodide yield respectively *de*-N-*methylbishydrocotarnine*, $C_{25}H_{30}O_6N_2$, m. p. 120—122° (*dihydriodide*, m. p.



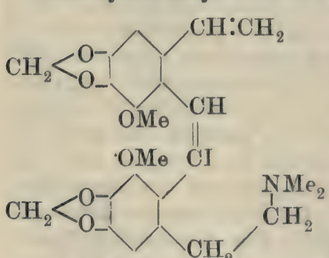
173—175°) and *de*-N-*methyliso-bishydrocotarnine*, m. p. 136° (*dihydriodide*, m. p. 146—149°), which are regarded as structural isomerides on account of their different chemical behaviour. Although their constitutions have not been definitely settled, that annexed is ascribed to de-*N*-methylbishydrocotarnine, because the substance reacts with bromine to form an additive *compound*, $C_{25}H_{30}O_6N_2Br_2$, m. p. 164—166°, which contains only one ionisable bromine atom. Both substances yield cotarnine by oxidation, and form only monomethiodides. *De*-N-*methylbishydrocotarnine methiodide*,



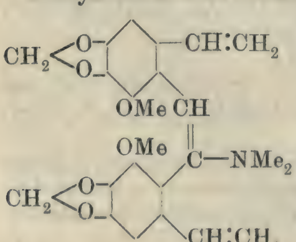
$C_{25}H_{30}O_6N_2,MeI$,

m. p. 151°, is decomposed by alcoholic sodium ethoxide yielding trimethylamine and *cotarnylidenehydrocotarnine* (annexed formula), m. p. 100—102° (decomp.). *De*-N-*methylisobishydrocotarnine methiodide*, $C_{25}H_{30}O_6N_2,MeI$, m. p. 159—162°, reacts with silver oxide and water and subsequently with potassium hydroxide to form a substance called *bis-de*-N-*methylisobishydrocotarnine*, $C_{26}H_{32}O_6N_2$, m. p. 218—220° (*hydriodide*, decomp. 248°), the *methiodide*, $C_{26}H_{32}O_6N_2,MeI$, m. p. 156—158°, of which is decomposed by sodium ethoxide, yielding trimethylamine and *cotarnylidene-de*-N-*methylhydrocotarnine* (see below).

Cotarnylidenehydrocotarnine yields cotarnine by oxidation, and forms with methyl iodide a substance, $C_{24}H_{26}O_6NI$, m. p. 115—117°, called *cotarnylidene-de-*N*-methyliodohydrocotarnine* (probable constitution annexed), which has pronounced basic properties (*hydriodide*, m. p. 209—211°), and yields by the evaporation of its solution in 50% alcohol the corresponding hydroxy-compound, *cotarnyl-de*-N-*methylhydroxycotarnine*, $C_{24}H_{27}O_7N$, m. p. 73—75° (*methiodide*, m. p. 160—162°).



Bishydrocotarnine dimethiodide, by treatment with silver oxide and water, and subsequently with boiling potassium hydroxide, yields *bis-de*-N-*methylbishydrocotarnine*, $C_{26}H_{32}O_6N_2$, m. p. 118—120° (*hydrobromide*, m. p. 166—168°; *hydriodide*, m. p. 160—162°), the *methiodide*, m. p. 113—115°, of which yields trimethylamine and *cotarnylidene-de*-N-*methylhydrocotarnine* (annexed formula), m. p. 68—71°, by treatment with alcoholic sodium ethoxide. The last-mentioned derivative does not react with methyl iodide.



A table is given showing the genetic relations of the preceding substances. C. S.

Alkaloids of Pareira Root. MAX SCHOLTZ (*Arch. Pharm.* 1911, **249**, 408—418. Compare Abstr., 1896, i, 710; 1899, i, 92; 1907, i, 79).—It has been shown already (*loc. cit.*) that pareira root contains either *l*- or *d*- bebeerine. A second alkaloid, chondrodine, has now been isolated from the total alkaloids of the root, and this paper deals with the isolation and characterisation of this substance, which may be regarded provisionally as a hydroxybebeerine.

Chondrodine, $C_{18}H_{21}O_4N$, m. p. 218—220°, $[\alpha]_D$ − 75° in alcohol, was obtained as an amorphous substance by a complicated process of separation from that portion of the total alkaloids which was insoluble both in ether and chloroform. The *hydrochloride*, B,HCl, m. p. 274—275°, crystallises in yellow leaflets; the *mercurichloride*, m. p. 288—290° (decomp.), is a crystalline powder; the *ferrichloride*, $B,HCl,FeCl_3$, m. p. 183—184°, occurs in microscopic crystals (?); the *perchlorate*, m. p. 232—233°, crystallises from hot water; the *picrate*, m. p. 193—194°, is a greenish-yellow, crystalline powder, and the *picrolonate*, m. p. 185—186°, forms greenish-yellow, stellate clusters of needles. The *methiodide*, m. p. 273° (decomp.), crystallises from water. The alkaloid contains a methoxyl and an ⁚NMe group. With acetic anhydride at 50—60° it furnishes an amorphous *diacetyl* derivative, which blackens above 270°. The *dibenzoyl* compound, m. p. 295°, separates from hot alcohol in crystalline granules. When heated with ethyl iodide in presence of alcohol and potassium hydroxide, chondrodine furnishes a *diethyl ether*, m. p. 205—207°, as a yellowish-white, sandy powder: the *hydrochloride* of this forms yellow needles and melts at 258°.

Bebeerine methiodide on further treatment with methyl iodide yields a *methyl ether*, $C_{16}H_{14}O(OMe)_2{\cdot}NMe_2I$, m. p. 263—264°, which separates from water as a yellow, crystalline powder. *Ethyl bebeerine*, m. p. 150°, obtained by the action of ethyl iodide on bebeerine in presence of potassium hydroxide and alcohol, is a colourless powder, soluble in alcohol, but not in ether; it is lævorotatory, $[\alpha]_D = -250°$ in alcohol, gives a crystalline *hydrochloride*, yellow leaflets, m. p. 109—110°, and furnishes a *methiodide*, m. p. 255—256°, which crystallises from hot water in needles. T. A. H.

Brucine Polyhydrosulphides. ERNST SCHMIDT and D. BRUNS (Reprint from *Apoth. Zeit.*, 1911, No. 67).—Schmidt has shown already (this Journ., 1876, ii, 94) that when hydrogen sulphide is passed through a solution of brucine in alcohol, a yellow and a red polyhydrosulphide are formed, to which the formulæ $B_3,H_2S_6,2H_2O$ and $B_3,2H_2S_6$ were assigned respectively. Doebner subsequently prepared (Abstr., 1895, i, 403) by the addition of ammonium polysulphide to brucine in alcohol, an orange-red polyhydrosulphide, to which he assigned the formula $B_2,H_2S_8,2H_2O$. It is now shown that Doebner's compound is identical with Schmidt's red polyhydrosulphide.

T. A. H.

Dihydroterpenylamine. George Francis Morrell (*Ber.*, 1911, **44**, 2560—2565).—When dihydrocarvylamine in dry ether is saturated with hydrogen chloride, at first at 0° and finally without cooling, an unstable *dihydrochloride*, $C_{10}H_{20}NCl,HCl$, white needles, m. p. 205°, is obtained. When this salt is heated with pyridine at 140—145°, it is converted into a *substance*, $C_{10}H_{19}N$, b. p. 96—100°/16 mm., $D_{16\cdot5}^{16\cdot5}$ 0·8909, $n_D^{16\cdot5}$ 1·49284 (*picrate*, m. p. about 176°), which is found to be a mixture of two stereoisomerides, α- and β-dihydroterpenylamine. Methods for their separation are indicated. *α-Dihydroterpenylamine*, b. p. 96—97°/15 mm., forms a *benzoyl* derivative, m. p. 219°, a suspension of which in glacial acetic acid is converted, by treatment with 10—12% ozone and subsequent heating on the water-bath, into acetone and a ketonic *substance*, $C_{14}H_{17}O_2N$, m. p. 183—185°, which is stated to be 2-benzoylamino-1-methyl*cyclo*hexan-4-one.

β-Dihydroterpenylamine, b. p. 100—101°/16 mm., forms more sparingly soluble salts than the α-base; the *nitrate*, m. p. 179° (decomp.), *picrate*, m. p. 195°, *hydrochloride*, m. p. 235° (decomp.), and *benzoyl* derivative, m. p. 178—179°, are described.

When a suspension of benzoyldihydrocarvylamine in acetic acid is ozonised and the product heated on the water-bath, a ketonic *substance*, $C_{16}H_{21}O_2N$, m. p. 218—219°, is obtained, which is regarded as 2-benzoylamino-4-acetyl-1-methyl*cyclo*hexane. C. S.

Action of Carbon Tetrabromide on Organic Bases. William M. Dehn and Albert H. Dewey (*J. Amer. Chem. Soc.*, 1911, **33**, 1588—1598).—Carbon tetrabromide unites with organic bases to form molecular compounds, the best results being obtained by mixing solutions of the substances in dry ether. In order to explain the mechanism of formation of these compounds, it is suggested that a "coalescence" first takes place, due to the residual valencies of the nitrogen and bromine, thus $\begin{array}{l}R\cdot NH_2\\ \;\;\vdots\\ Br\cdot CBr_3\end{array}$, and that this is followed by a shifting of the bonds, as shown by the formula $\begin{array}{c}R\cdot NH_2\\ \diagup\diagdown\\ Br\;\;CBr_3\end{array}$. In the case of pyridine and piperidine, one molecule of the base unites with two molecules of carbon tetrabromide. It is evident that these two molecules are held with different degrees of tenacity, since vapour-pressure curves indicate a dissociation of one molecule at 100°, and of the second molecule between 100° and 210°. Moreover, the complex compound is decomposed by water in accordance with the equation: $C_5H_7N,2CBr_4 + 2H_2O \longrightarrow CBr_4 + CO_2 + 3HBr + C_5H_7N,HBr$. The pyridine compound therefore has the structure: $\begin{array}{l}C_5H_5N\cdot CBr_3\\ \qquad\;\; | \\ \qquad Br\colon Br\cdot CBr_3\end{array} \longrightarrow$

$$\begin{array}{l}C_5H_5N\cdot CBr_3\\ \qquad | \\ \;\;Br\cdot Br\cdot CBr_3\end{array}, \text{ or } \begin{array}{l}C_5H_5N\cdot Br\\ \qquad | \\ \;\;Br_2C\cdot Br\colon Br\cdot CBr_3\end{array} \longrightarrow \begin{array}{l}C_5H_5N\cdot Br\\ \qquad | \\ \;\;Br_2C\cdot Br\cdot CBr_3.\\ \qquad\quad | \\ \qquad\quad Br\end{array}$$

The *piperidine* compound, $C_5H_{11}N,2CBr_4$, m. p. 148°, crystallises in prismatic needles. The *pyridine* compound, $C_5H_5N,2CBr_4$, m. p. 218—220°, D^{21} 2·70, forms iridescent crystals, and is not decomposed

by boiling alcohol. The *quinoline* compound, C_9H_7N,CBr_4, m. p. 142°, crystallises in white, prismatic needles. The 2-*picoline* compound, $C_6H_7N,2CBr_4$, m. p. 214°, forms large needles. With 2 : 6-lutidine, a product, m. p. 106°, was obtained in clusters of short needles; this may have been either the compound, $C_5H_3Me_2N,CBr_4$, or a mixture of the compound $C_5H_3Me_2N,2CBr_4$ with lutidine hydrobromide. Carbon tetrabromide reacts with phenylhydrazine with evolution of nitrogen and formation of bromoform and phenylhydrazine hydrobromide. On the addition of carbon tetrabromide to benzylamine, benzylamine hydrobromide separates. Di*iso*amylamine and dipropylamine yield products which are probably mixtures of the carbon tetrabromide compound with the hydrobromide of the base. With ethylamine, ethylamine *hydrobromide*, m. p. 157°, and the *compound*, $4NH_2Et,CBr_4$, m. p. 150°, are produced.

The following salts were obtained during the course of this work. Piperidine *auribromide*, m. p. 242°; pyridine *auribromide*, m. p. 319°; quinoline *hydrobromide*, m. p. 62—65°, and *auribromide*, m. p. 209°; picoline *auribromide*, m. p. 209°; 2 : 6-lutidine *hydrobromide*, m. p. 114°, and *auribromide*, m. p. 180°; benzylamine *auribromide*, m. p. 178°; and ethylamine *auribromide*, m. p. 190°. E. G.

Homologous Nature of Anthranil and Methylanthranil. JOHANNES SCHEIBER (*Ber.*, 1911, **44**, 2409—2418).—The question whether anthranil, $C_6H_4<\begin{matrix}CO\\ |\\ NH\end{matrix}$ or $C_6H_4<\begin{matrix}CH\\ |\\ N\end{matrix}>O$, and methylanthranil, $C_6H_4<\begin{matrix}CMe\\ |\\ N\end{matrix}>O$, are homologous has very frequently been the subject of discussion. It is shown by measurement of the ultra-violet absorption that the two compounds behave absolutely identically, and are therefore homologous.

Heller (Abstr., 1908, i, 267; 1909, i, 832) has shown that anthranil and methylanthranil behave differently towards 23% hydrochloric acid and sodium nitrite, but that they behave similarly when 39% acid is used. Measurements of the ultra-violet absorption of the two compounds in acids of these strengths show them to be identical in 4·9% acid, to differ in 24·5% acid, and to be identical again in 39% acid. Anthranil is shown to be very stable towards hydrogen chloride, and the change in absorption is not due to an opening of the ring. When kept for twelve days in 4·9% acid solution, anthranil gives slightly different curves; those for methylanthranil correspond with the readings taken immediately on dissolution.

Anthroxanic acid, $C_6H_4<\begin{matrix}C(CO_2H)\\ |\\ N\end{matrix}>O$, likewise shows the same ultra-violet absorption as the two anthranils. The absorption in this case is not altered by solution in hydrochloric acid; possibly the alteration in the case of the homologous anthranils is due to salt formation. E. F. A.

Constitution of the ψ-Bases of Quinoline. II. ADOLF KAUFMANN and J. M. PLÁ Y JANINI (*Ber.*, 1911, **44**, 2670—2677).—Kaufmann and Strübin (this vol., i, 321) have recently obtained

experimental evidence in support of the view that the pseudo-bases (quinolanols) of the quinoline series slowly undergo transformation into the isomeric *o*-alkylaminocinnamaldehydes, owing to the rupture of the pyridine ring. According to this view, 2-substituted quinoline bases should give rise to derivatives of cinnamic acid. The present paper contains an account of the reactions of 2-hydroxy-2-phenyl-1-methylquinoline (I) and its transformation into phenyl *o*-methylaminostyryl ketone (II):

$$C_6H_4<\begin{matrix}CH{=}CH \\ NMe\cdot CPh\cdot OH\end{matrix} \quad \longrightarrow \quad C_6H_4<\begin{matrix}CH{:}CH\cdot COPh \\ NHMe\end{matrix}.$$

(I.) (II.)

2-Phenylquinoline methiodide (Doebner and Miller, Abstr., 1886, 721) is best prepared by the action of magnesium phenyl bromide on quinoline methiodide and subsequent oxidation of the resulting 2-phenyl-1-methyl-1 : 2-dihydroquinoline (compare Freund, Abstr., 1905, i, 156) with alcoholic iodine; its solution in water is colourless, in alcohol yellow, and in chloroform orange-red. When treated with aqueous sodium hydroxide, it yields the corresponding ψ-base (Decker and Fellenberg, Abstr., 1907, i, 1064), which is converted by the action of aqueous hydrochloric acid on its benzene solution into 2-*phenylquinoline methochloride*. This crystallises in long, almost colourless needles, which begin to decompose at 170°, and melt at 195—200° to a clear liquid; it is identical with the compound obtained by the interaction of silver chloride and 2-phenylquinoline methiodide. When treated with aniline and potassium hydroxide, the methiodide yields *phenyl* o-*methylaminostyryl ketoneanil*,

$$NHMe\cdot C_6H_4\cdot CH{:}CH\cdot CPh{:}NPh,$$

which crystallises in greenish-yellow needles, melting at 140° to a green liquid. The anil is unstable, and readily decomposes when heated alone or in benzene solution, yielding a green dye. It is hydrolysed by cold mineral acids into its components; thus, with hydrochloric acid, it yields aniline and 2-phenylquinoline methochloride.

An alkaline suspension of the above-mentioned ψ-base is oxidised by exposure to air, or more rapidly by potassium ferricyanide, to *ω-benzoyl-*o*-methylaminoacetophenone* (III), which crystallises from benzene in stout needles, m. p. 123°. The latter compound dissolves in acids, yielding salts of 4-keto-2-phenyl-1-methyl-3 : 4-dihydroquinolium hydroxide (IV); the *chloride*, $C_{16}H_4ONCl$, crystallises in stellar aggregates of almost colourless needles, m. p. 237° (decomp.); the *iodide* is light yellow, m. p. 220°; the *picrate*, $C_{22}H_{16}O_8N_4$, forms yellow crystals, m. p. 180°. The salts are reconverted by the action of sodium carbonate or ammonia, or even by boiling with water, into ω-benzoyl-*o*-methylaminoacetophenone, as represented in the following scheme:

$$C_6H_4<\begin{matrix}CO\cdot CH_2\cdot COPh \\ NHMe\end{matrix} \quad \underset{\text{Alkali}}{\overset{\text{HCl}}{\rightleftarrows}} \quad C_6H_4<\begin{matrix}CO \text{——} CH_2 \\ NMeCl{:}CPh\end{matrix}.$$

(III.) (IV.)

When heated at 250—260°, the chloride loses methyl chloride, yielding 4-hydroxy-2-phenylquinoline, m. p. 256° (Conrad and Limpach, Abstr.,

1888, 505), which is transformed by distillation with zinc dust into 2-phenylquinoline, and by the action of phosphorus pentachloride into 4-chloro-2-phenylquinoline (Knorr and Fertig, Abstr., 1897, i, 371). An explanation is also given of the oxidation of 4-cyano-1-alkyl-dihydroquinolines to 4-cyano-1-alkyl-2-quinolones, observed by Kaufmann and Albertini (Abstr., 1909, i, 958). It is assumed that the hydrogen in the 4-position is first oxidised to hydroxyl with the formation of the compound (V), which then undergoes transformation into (VI) by the addition of water and simultaneous rupture of the pyridine ring:

$$C_6H_4<\begin{matrix}C(CN)(OH)\cdot CH \\ NR\text{———}CH\end{matrix} \longrightarrow C_6H_4<\begin{matrix}C(CN)(OH)\cdot CH_2\cdot CHO \\ NHR\end{matrix};$$

(V.) (VI.)

4-cyano-1-alkyl-2-quinolones are formed from this intermediate product by oxidation and loss of two molecules of water. The above-mentioned formation of ω-benzoyl-*o*-methylaminoacetophenone may be explained in a similar manner. F. B.

Condensation Products of Isatic Acid and Hydroxythionaphthen, Indandione, and Indanone. EMILIO NOELTING and ALEX. HERZBAUM (*Ber.*, 1911, **44**, 2585—2590).—Isatin in alkaline solution reacts with hydroxythionaphthen, indandione, or indanone just as with indoxyl (Noelting and Steuer, this vol., i, 165), yielding the following substances in accordance with the scheme:

$$C_6H_4<\begin{matrix}CO \\ X\end{matrix}>CH_2 + NH_2\cdot C_6H_4\cdot CO\cdot CO_2H \longrightarrow$$

$$C_6H_4<\begin{matrix}N\text{====}C\text{—} \\ C(CO_2H):C\cdot X\end{matrix}>C_6H_4,$$

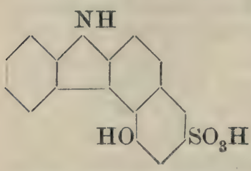
where X = S, CO, or CH_2. Thus hydroxythionaphthen yields "*thioquindolinecarboxylic acid*," $C_{16}H_9O_2NS$, yellow needles, which decomposes above its m. p., about 335°, forming "thioquindoline," m. p. 172° (not 169°, *loc. cit.*). Indandione yields *quinolylenephenyleneketonecarboxylic acid*, $C_{17}H_9O_3N$, colourless needles, which is converted into the corresponding ketone (Noelting and Blum, Abstr., 1901, i, 728) above its m. p., about 340°. Indanone yields *quinolylenephenylenemethanecarboxylic acid*, $C_{17}H_{11}O_2N$, m. p. 330° (decomp), which is converted by fusion into quinolylenephenylenemethane (Noelting and Blum, *loc. cit.*); the latter has also been obtained by condensing indanone and *o*-aminobenzaldehyde in boiling dilute hydrochloric acid.

The sodium salts of the three preceding acids yield with metallic salts precipitates, the colours of which are tabulated. C. S.

[Preparation of Carbazole Derivatives.] KALLE & Co. (D.R.-P. 234338).—Carbazole derivatives obtained from 6-amino-1-naphthol-3-sulphonic acid and hydrazines have previously been described, and the reaction has now been extended to the case of 7-amino-1-naphthol-3-sulphonic acid.

The carbazole, 1-*hydroxybenzo-β-naphthindole-3-sulphonic acid*

(annexed formula), is prepared by heating this acid in aqueous solution with phenylhydrazine in the presence of sodium hydrogen sulphite and sodium hydroxide; on cooling, the carbazole separates in microcrystalline form.



The action is stated to be widely applicable, both with regard to the acid and hydrazine or other aromatic base employed.

The dyes obtained from tetrazotised benzidine, coupled with the foregoing carbazole (1 mol.) and salicylic acid and resorcinol respectively, are described in the original. F. M. G. M.

Action of Hydroxylamine on Ketones of the Type R·CH:CH·CH:CH·COPh. ROBERTO CIUSA and A. TERNI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 25—30. Compare Abstr., 1908, i, 762; Ciusa and Bernardi, Abstr., 1910, i, 684).—The present paper is concerned with the further examination of α-cinnamylideneacetophenonehydroxylamineoxime, previously described.

Benzylidene-α-cinnamylideneacetophenonehydroxylamineoxime,

$$C_{24}H_{22}O_2N_2,$$

is obtained by boiling for one hour alcoholic solutions of benzaldehyde and the hydroxylamineoxime; it has m. p. 175°.

α-Cinnamylideneacetophenonehydroxylamineoxime, when oxidised with permanganate, yields benzoic acid and a 3-*phenyl*-5-*styryl*iso-*oxazole*, $\begin{matrix} \mathrm{CH{\cdot}CPh} \\ \mathrm{CHPh{:}CH{\cdot}C\text{——}O} \end{matrix}\!\!>\!N$, which forms lustrous scales, m. p. 138°. The hydroxylamineoxime yields with nitrous acid (sodium nitrite and glacial acetic acid in the cold) an isomeride of α-cinnamylideneacetophenoneoxime, m. p. 124°, identical with the substance previously obtained among the secondary products of the reaction between cinnamylideneacetophenone and hydroxylamine (compare Ciusa and Terni, *loc. cit.*). To this substance the constitution of a 3-*phenyl*-5-*styryldihydro*iso*oxazole*, $\begin{matrix} \mathrm{CH_2{\cdot}CPh} \\ \mathrm{CHPh{:}CH{\cdot}CH\text{——}O} \end{matrix}\!\!>\!N$, is ascribed. It yields a *dibromo*-derivative, $C_{17}H_{15}ONBr_2$, which crystallises in small, colourless needles, m. p. 145°. When α-cinnamylideneacetophenonehydroxylamineoxime is boiled with 90% acetic acid or normal hydrochloric acid, it gives the α-oxime of m. p. 135°. This explains the fact that when hydroxylamine hydrochloride reacts with unsaturated ketones in the absence of sodium acetate only oximes, and not hydroxylamineoximes, are obtained (compare Ciusa and Bernardi, *loc. cit.*). R. V. S.

Aromatic ψ-Thiocarbamides and their Conversion into Aryl *ortho*-Thiocarbonates. FRITZ ARNDT (*Annalen*, 1911, **384**, 322—351). —The interaction of *p*-tolyl mercaptan and cyanamide, with the addition of ether to moderate the violence of the reaction, gives an almost quantitative yield of p-*tolyl*-ψ-*thiocarbamide*,

$$NH{:}C(NH_2){\cdot}S{\cdot}C_7H_7,$$

m. p. 110° (decomp.). The substance decomposes when heated alone

or in boiling alcohol, yielding *p*-tolyl mercaptan and dicyanodiamide It forms a *dibenzoate*, $NBz\!:\!C(NHBz)\cdot S\cdot C_7H_7$, m. p. 122—123°, with benzoyl chloride in cold pyridine, and also yields well crystallised salts, of which the *acetate, sulphate, chromate, chloride*, and *nitrate*, m. p. 173°, are described. Very characteristic is its behaviour in the presence of nitric and sulphuric acids, whereby a *nitrate-sulphate*,

$$3C_8H_{10}N_2S,H_2SO_4,HNO_3,$$

is obtained, even when the dilution of the nitric acid is one in 100,000; provided an excess of the reagent is present, this salt is so insoluble that it can be employed for the estimation of nitrates. Similar, sparingly soluble double salts are obtained in the presence of sulphuric acid and the majority of the monobasic acids or hydroferrocyanic acid, but not hydroferricyanic acid, hydrogen cyanide, phosphoric acid, or organic acids; however, the place of the sulphuric acid cannot be taken by any other acid. (The isomeric benzyl-ψ-thiocarbamide does not form double salts corresponding with the preceding.)

p-Tolyl-ψ-thiocarbamide chloride or acetate reacts with concentrated sodium nitrate (not potassium nitrite) in neutral solution to form the *nitrite*, m. p. 112°, but in the presence of hydrochloric acid, *nitroso*-p-*tolyl-ψ-thiocarbamide*, $C_8H_9ON_3S$, decomp. 112°, is obtained, which receives the constitution $C_7H_7S\cdot C(\!:\!NH)\cdot NH\cdot NO$ or

$$C_7H_7S\cdot C(\!:\!NH)\cdot N\!:\!N\cdot OH$$

on account of its absence of colour, insolubility in dilute acids, response to the Liebermann test, and conversion by glacial acetic acid into nitrogen and *p*-tolyl thiocyanate. When the nitroso-compound is recrystallised from methyl alcohol without the addition of a little ammonia, it is partly converted into a yellow *substance*, decomp. about 130°, which is probably $C_7H_7S\cdot CO\cdot NH\cdot NO$.

When its methyl-alcoholic solution is warmed with aqueous ammonia, nitroso-*p*-tolyl-ψ-thiocarbamide is converted into p-*tolyl orthothiocarbonate*, $C(S\cdot C_7H_7)_4$, needles, m. p. 147°, which forms with bromine in chloroform an unstable *perbromide*, $C(S\cdot C_7H_7)_4,Br_8$, dark red leaflets, m. p. below 100° (of freshly prepared specimen), which readily changes to a yellow, crystalline *tetrabromide*, $C(S\cdot C_7H_7)_4,Br_4$, m. p. 169°. By boiling the tetrabromide with alcohol or warming the thiocarbonate itself with acetic and a little concentrated sulphuric acid, the *disulphoxide*, $C(S\cdot C_7H_7)_2(SO\cdot C_7H_7)_2$, m. p. 92°, is obtained. An attempt to synthesise *p*-tolyl orthothiocarbonate from sodium *p*-tolylmercaptide and carbon tetrachloride in boiling alcohol resulted in the formation of p-*tolyl orthothioformate*, $CH(S\cdot C_7H_7)_3$, m. p. 111°, which is also produced by the reduction of the orthothiocarbonate by zinc and acetic acid.

Benzyl-ψ-thiocarbamide and sodium nitrite react in acid solution to form a stable *nitrite*, m. p. 126° (decomp.), which yields benzyl disulphide by heating; a substance corresponding with nitroso-*p*-tolyl-ψ-thiocarbamide is not formed.

p-Tolyl mercaptan and phenylcyanamide react in ether to form *phenyl*-p-*tolyl-ψ-thiocarbamide*, $NHPh\cdot C(NH)\cdot S\cdot C_7H_7$, m. p. 148°, which forms a *hydrochloride*, *nitrate*, m. p. 132°, and *benzoyl* derivative, m. p. 151·5°, and is easily methylated, yielding *phenyl*-p-*tolylmethyl-ψ-thiocarbamide*, $NPhMe\cdot C(NH)\cdot S\cdot C_7H_7$, m. p. 121°.

Diphenyl-p-*tolyl*-ψ-*thiocarbamide*, $NHPh\cdot C(NPh)\cdot S\cdot C_7H_7$, m. p. 119—120°, is obtained by desulphurising diphenylthiocarbamide in benzene by mercuric oxide and treating the resulting solution of carbodiphenylimide with *p*-tolyl mercaptan.

Hofmann's triphenyl*iso*melamine, m. p. 185° (Abstr., 1886, 233), is shown to be an additive compound of triphenylmelamine and phenylcyanamide; the former constituent can be removed by dilute acid or boiling water. C. S.

Conversion of Nitroaldehydes into Cyanoaldehydes. GIACOMO PONZIO (*Gazzetta*, 1911, 41, i, 787—793. Compare Ponzio and Giovetti, Abstr., 1910, i, 194).—The author has shown previously that an aliphatic nitro-group may be substituted by $-NH_2$ or $-NHPh$ (compare Abstr., 1910, i, 339, 442, 699), and he now finds that it may also be replaced by $-CN$. A new method of preparation is thus provided for the hydrazones of ω-cyanobenzaldehyde, which, although longer than that formerly given, has the advantage that the *o*- and *m*-substituted phenylhydrazones can also be obtained.

ω-Cyanobenzaldehyde-*o*-nitrophenylhydrazone (*loc. cit.*) is the only substance produced when ω-nitrobenzaldehyde-*o*-nitrophenylhydrazone is boiled for two hours in aqueous alcoholic solution with potassium cyanide.

ω-Cyanobenzaldehyde-m-*nitrophenylhydrazone*,

$$CN\cdot CPh:N\cdot NH\cdot C_6H_4\cdot NO_2,$$

which cannot be obtained by the method formerly given, crystallises in small, yellow prisms, m. p. 197—198°. It is soluble in alkali to which a drop of alcohol has been added, and it gives a yellow coloration. The *ω-nitrobenzaldehyde*-m-*nitrophenylhydrazone* employed for its preparation is obtained by heating the sodium salt of ω-nitrotoluene with *m*-nitrobenzenediazonium sulphate; it crystallises in small, brick-red prisms, m. p. 132° (decomp.).

ω-Cyanobenzaldehyde-*p*-nitrophenylhydrazone, ω-cyanobenzaldehyde-*o*-chloro-*p*-nitrophenylhydrazone, and ω-cyanobenzaldehyde-*o*-*p*-dinitrophenylhydrazone can also be prepared by the new method. The *ω-nitrobenzaldehyde*-o-p-*dinitrophenylhydrazone* necessary for the preparation of the last-named substance is obtained by diazotising 2 : 4-dinitroaniline and acting on the sodium salt of ω-nitrotoluene with the 2 : 4-dinitrobenzenediazonium sulphate so produced. The substance crystallises in yellowish-brown, flat needles, m. p. 152° (decomp.). R. V. S.

Syntheses of Pyrazolones from a Derivative of γ-Pyrone. F. CARLO PALAZZO and RAFFAELE LIVERANI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 55—60. Compare Palazzo, Abstr., 1906, i, 701).—By the action of hydrazine hydrate on ethyl dimethylpyronedicarboxylate the authors have obtained three different nitrogenous compounds, which all belong to the pyrazolone group. When 1 mol. of hydrazine hydrate is boiled with the ester in methyl-alcoholic solution for two minutes, a small quantity (2%) of a compound is obtained, which crystallises in minute needles, m. p. 195—196°, and gives a reddish-violet coloration with ferric chloride. Of this substance

no analysis could be made, but it is identical with the product $C_7H_{10}O_3N_2$, from hydrazine hydrate and ethyl acetylmalonate, which is shown to be 3-*methyl-5-pyrazolone-4-carboxylate.* When two mol. of hydrazine hydrate are heated in a sealed tube with a concentrated methyl-alcoholic solution of ethyl dimethylpyronedicarboxylate for some hours at 120°, a *substance*, $C_5H_5O_2N_2{\cdot}OEt$, is obtained in good yield. The compound has m. p. 125—130° (softening considerably at 50—60°), and gives a reddish-brown coloration with ferric chloride. It is suggested that it may be an isomeride of the first-mentioned compound. By the interaction of two mols. of hydrazine hydrate and ethyl dimethylpyronedicarboxylate in methyl-alcoholic solution as before, the mixture being boiled for two hours, a *substance* is produced, which has m. p. 142—145°. It gives a reddish-brown coloration with ferric chloride. The analytical results agree with the formula $C_{11}H_{16}O_4N_4$, but the substance appears to be a mixture, possibly of equimolecular amounts of the two pyrazolones, $C_7H_{10}O_3N_2$ and $C_4H_6ON_2$. R. V. S.

The Pyrazoline Transformation of Unsaturated Hydrazones. Hugo Bauer and Hedwig Dieterle (*Ber.*, 1911, 44, 2697—2702).—It has been shown by Auwers (Abstr., 1909, i, 59; 1910, i, 70) that the phenylhydrazones of many unsaturated ketones may be transformed into pyrazoline derivatives by heating them with glacial acetic acid. That the reaction is, however, not a general one has been confirmed by the authors from an examination of the behaviour of unsaturated ketones of the type CHPh:CH·CH:CH·CO·CH:CHR. When R = anisyl or furyl, the action of phenylhydrazine leads directly to the formation of a pyrazoline derivative; the intermediately formed phenylhydrazones could not be isolated. On the other hand, when R = phenyl, the phenylhydrazone is not converted into a pyrazoline derivative, even by prolonged heating with acetic acid.

1-*Phenyl-3-β-styrylvinyl-5-anisylpyrazoline*,

$$CHPh{:}CH{\cdot}CH{:}CH{\cdot}C{\lessdot}\genfrac{}{}{0pt}{}{-CH_2-}{N{\cdot}NPh}{\gtrdot}CH{\cdot}C_6H_4{\cdot}OMe,$$

prepared by heating anisylidenecinnamylideneacetone [*p*-methoxystyryl β-styrylvinyl ketone] with phenylhydrazine in glacial acetic acid solution, forms yellow crystals, m. p. 155—156°; its alcoholic solution has an intense, green fluorescence. When oxidised with aqueous potassium permanganate, it yields benzoic acid and 1-*phenyl-5-anisylpyrazole-3-carboxylic acid*, $OMe{\cdot}C_6H_4{\cdot}C{\lessdot}\genfrac{}{}{0pt}{}{CH\text{——}}{NPh{\cdot}N}{\gtrdot}C{\cdot}CO_2H$, which crystallises from water in white needles, m. p. 178—179°, and yields a *copper* salt, $(C_{17}H_{15}O_3N_2)_2Cu$, crystallising in slender, green needles. The formation of this acid proves that the double linking, adjacent to the anisyl group, is concerned in the pyrazoline formation, and this is confirmed by the behaviour of the two following phenylhydrazones, which do not contain a double linking in this position, and, therefore, are not transformed into pyrazoline derivatives.

ζ-Bromo-η-methoxy-a-phenyl-η-anisyl-$\Delta^{a\gamma}$-heptadien-ε-onephenylhydrazone, CHPh:CH·CH:CH·C(N·NHPh)·CHBr·CH(OMe)·C_6H_4·OMe,

obtained from the corresponding ketone (this vol., i, 881) and phenylhydrazine, has m. p. 201—202·5°.

γδζ-Tribromo-η-methoxy-α-phenyl-η-anisyl-Δ^{a}-hepten-ε-onephenylhydrazone, $CHPh{:}CH{\cdot}[CHBr]_2{\cdot}C(N{\cdot}NHPh){\cdot}CHBr{\cdot}CH(OMe){\cdot}C_6H_4{\cdot}OMe$, also prepared from the corresponding ketone (*loc. cit.*), forms slender, yellow needles, m. p. 181—182°.

Styryl β-styrylvinyl ketonephenylhydrazone,

$$CHPh{:}CH{\cdot}CH{:}CH{\cdot}C({:}N{\cdot}NHPh){\cdot}CH{:}CHPh,$$

prepared from its components in alcoholic solution, crystallises in yellowish-brown platelets, m. p. 111—112°.

Furfurylidenecinnamylideneacetone [*β-styryl-β′-furyldivinyl ketone*],

$$CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}C_4H_3O,$$

obtained by the condensation of furfuraldehyde with cinnamylideneacetone (β-styrylvinyl methyl ketone) by means of sodium hydroxide in aqueous alcoholic solution, crystallises in lustrous, golden-yellow leaflets, m. p. 97—98°. It gives an intense red coloration with strong nitric acid, and is transformed by the action of pnenylhydrazine into 1-*phenyl*-3-*β-styrylvinyl*-5-*furylpyrazoline*,

$$CHPh{:}CH{\cdot}CH{:}CH{\cdot}C{\lessgtr}\begin{matrix}-CH_2-\\N{\cdot}NPh\end{matrix}{>}CH{\cdot}C_4H_3O,$$

which crystallises in strongly fluorescent, slender, yellow needles, m. p. 165—166°, and is oxidised by aqueous permanganate to benzoic acid and 1-*phenylpyrazole*-3 : 4-*dicarboxylic acid*, m. p. 250—255°.

F. B.

Hydantoins. IV. 2-Thio-1-phenylhydantoins from Some α-Amino-acids. Charles A. Brautlecht (*J. Biol. Chem.*, 1911, 10, 139—146. Compare Wheeler and Brautlecht, this vol., i, 500).—The action of phenylthiocarbimide on a number of α-amino acids has been studied. In the presence of alkali, interaction takes place with the formation of alkali salts of thiohydantoic acids. These readily undergo transformation into the corresponding hydantoins on treatment with hydrochloric acid. Crystalline thiophenylhydantoins could not, however, be obtained from cystine and α-pyrrolidonecarboxylic acid.

These thiophenylhydantoins are characteristic of the α-amino-acids, and should serve for their identification. When warmed with potassium hydroxide, they are hydrolysed to the potassium salts of the thiohydantoic acids. They are desulphurised by digestion in aqueous or dilute alcoholic solutions with silver nitrate, mercuric chloride, etc., and are stable in the presence of boiling hydrochloric acid.

2-Thio-1-phenylhydantoin, $CS{<}\begin{matrix}NPh{\cdot}CO\\NH-CH_2\end{matrix}$, from glycine has m. p. 240—242°.

2-*Thio*-1-*phenyl*-4-*ethylhydantoin* from α-amino-*n*-butyric acid crystallises in plates, m. p. 190—192°.

2-*Thio*-1-*phenyl*-4-iso*propylhydantoin*, obtained from valine, forms colourless needles, m, p. 206—208°.

2-*Thio*-1-*phenyl*-4-*benzylhydantoin* from phenylalanine separates in colourless prisms, m. p. 187°.

Tyrosine gives rise to 2-*thio*-1-*phenyl*-4-p-*hydroxybenzylhydantoin*, colourless or straw-coloured prisms, m. p. 214—216°.

From asparagine 2-*thio*-1-*phenylhydantoin*-4-*acetamide* is obtained; it crystallises in colourless, lenticular prisms, m. p. 234°.

The *potassium* salt of the hydantoic acid,

$$NHPh\cdot CS\cdot NH\cdot CH(CO_2K)\cdot CH_2\cdot CO\cdot NH_2,$$

separates in colourless plates, m. p. 154°.

2-*Thio*-1-*phenylhydantoin*-4-*acetic acid*, $\begin{matrix} NPh\cdot CO \\ | \\ CS-NH \end{matrix}\!\!>\!CH\cdot CH_2\cdot CO_2H$, from aspartic acid crystallises in colourless prisms, m. p. 233—234° (decomp.).

2-*Thio*-1-*phenylhydantoin*-4-*propionic acid*, prepared from glutamic acid, separates in microscopic needles, m. p. 169—170°. E. F. A.

Hydantoins. V. Synthesis of 3 : 5-Dichlorotyrosine. HENRY L. WHEELER, CHARLES HOFFMAN, and TREAT B. JOHNSON (*J. Biol. Chem.*, 1911, 10, 147—157).—Tyrosine itself does not react smoothly with chlorine, but tyrosinehydantoin reacts with chlorine in glacial acetic acid solution, forming the corresponding *hydantoin* of 3 : 5-*dichlorotyrosine*. The same compound was obtained on reducing 3 : 5-dichlorobenzylidenehydantoin with hydriodic acid, a compound which was prepared by Wheeler and Hoffmann (this vol., i, 498) by condensation of hydantoin with 3 : 5-dichlorobenzaldehyde. Chlorine therefore is substituted in the same positions (3 : 5) in the benzene nucleus of tyrosinehydantoin as are taken by iodine and bromine when they combine with tyrosine. On digestion with barium hydroxide, the hydantoin is converted into 3 : 5-*dichlorotyrosine*. This crystallises with $2H_2O$, dissociates in aqueous solution, and reacts acid to litmus; it does not give a red coloration with Millon's reagent.

Benzylidenehydantoin reacts with chlorine and bromine in acetic acid, forming *a-chloro-* and *a-bromo-benzylidenehydantoin* respectively. The latter is reduced by hydriodic acid, forming benzylhydantoin. Anisylidenehydantoin was not reduced under practically the same conditions.

3 : 5-*Dichlorotyrosinehydantoin* crystallises in rhombohedral prisms, m. p. 202° (decomp.).

3 : 5-*Dichlorotyrosine* separates in rectangular, prismatic crystals, m. p. 252° (decomp.). The *hydrochloride* forms large, prismatic, colourless crystals, m. p. 260—265° (decomp.).

a-Bromobenzylidenehydantoin, $\begin{matrix} NH\cdot CO \\ | \\ CO\cdot NH \end{matrix}\!\!>\!C\!:\!CBrPh$, crystallises in plates, m. p. 240° to an oil.

a-Thiolbenzylidenehydantoin, prepared by boiling the bromo-compound with potassium hydrosulphide, crystallises in yellow prisms, m. p. 199° (decomp.).

a-Chlorobenzylidenehydantoin also crystallises in plates, m. p. 273° to an oil.

p-*Methoxybenzylhydantoin*, prepared by reduction of anisylidenehydantoin (Wheeler and Hoffman, *loc. cit.*), crystallises in yellow, hexagonal tablets, m. p. 174° to a clear oil. Anisylidenehydantoin could not be reduced with tin and hydrochloric acid; after boiling

with zinc and acetic acid, it was recovered unchanged, but in a colourless form. Digestion with sodium hydroxide converts it into *p*-methoxyphenylpyruvic acid. E. F. A.

Pyrimidines. LIII. Condensation of Ethyl Formate and Ethyl Oxalate with Some Pyrimidinethioglycollates. Treat B. Johnson and Norman A. Shepard (*Amer. Chem. J.*, 1911, 46, 345—361).—The work described was undertaken with the object of obtaining further knowledge of the behaviour of the grouping $-S \cdot CH_2 \cdot CO-$. Johnson and Guest (Abstr., 1909, i, 744) have studied the condensation of ethyl formate with ethyl benzylthiolacetate, and Hinsberg (Abstr., 1910, i, 334) has shown that the methylene groups in ethyl thiodiglycollate react readily with α-dicarbonyl compounds.

The only pyrimidine derivative of ethyl thiolacetate hitherto described is ethyl 1 : 6-dihydro-6-pyrimidone-2-thiolacetate, which was obtained by Wheeler and Liddle (Abstr., 1909, i, 61) by the action of ethyl chloroacetate on 2-thiouracil. It is now shown that trans-β-*thiocarbaminoacrylic acid*, $NH_2 \cdot CS \cdot NH \cdot CH \colon CH \cdot CO_2H$, which forms lustrous plates and does not melt below 300°, is also produced in this reaction.

Ethyl 1 : 6-dihydro-6-pyrimidone-2-thiolacetate condenses with ethyl formate in presence of sodium ethoxide with formation of *ethyl* 1 : 6-*dihydro*-6-*pyrimidone*-2-α-*thiol*-β-*hydroxyacrylate*,

$$NH<\begin{matrix}C[S \cdot C(CH \cdot OH) \cdot CO_2Et] \colon N \\ CO\text{———————————}CH\end{matrix}>CH,$$

m. p. 138—140°, which crystallises in prisms.

By the condensation of ethyl oxalate with 1 : 6-dihydro-6-pyrimidone-2-thiolacetate, *diethyl* 1 : 6-*dihydro*-6-*pyrimidone*-2-*thioloxalylacetate*, $NH<\begin{matrix}C[S \cdot CH(CO \cdot CO_2Et) \cdot CO_2Et] \colon N \\ CO\text{————————————}CH\end{matrix}>CH$, m. p. 171°, is obtained, which crystallises in stout blocks, and is decomposed by hydrochloric acid with formation of 1 : 6-*dihydro*-6-*pyrimidone*-2-*thiolpyruvic acid*, $NH<\begin{matrix}C(S \cdot CH_2 \cdot CO \cdot CO_2H) \colon N \\ CO\text{—————————}CH\end{matrix}>CH$, m. p. 200—201° (decomp.); it is also decomposed by potassium hydroxide with production of uracil.

When ethyl 1 : 6-dihydro-6-pyrimidone-2-α-thiol-β-hydroxyacrylate is heated with thiocarbamide in presence of sodium ethoxide, 2(*tetrahydro*-2′-*thio*-6′-*pyrimidonethiol*)-1 : 6-*dihydro*-6-*pyrimidone*,

$$CS<\begin{matrix}NH-CO \\ NH \cdot CH\end{matrix}>C \cdot SC<\begin{matrix}NH \cdot CO \\ N-CH\end{matrix}>CH,$$

is produced, which crystallises in needles and decomposes at 285—295°. Thiocarbamide also condenses with ethyl 1 : 6-dihydro-6-pyrimidone-2-thioloxalylacetate with formation of small quantities of a compound which is probably identical with that just described.

Ethyl 4-*methyl*-1 : 6-*dihydro*-6-*pyrimidone*-2-*thiolacetate*,

$$NH<\begin{matrix}C(S \cdot CH_2 \cdot CO_2Et) \colon N \\ CO\text{—————————}CH\end{matrix}>CMe,$$

m. p. 145—146°, obtained by the action of ethyl chloroacetate on 2-thio-4-methyluracil, forms colourless needles; the corresponding *acid*, m. p. 192—197° (decomp.), crystallises in colourless prisms; the *potassium* salt is described.

When ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolacetate is heated with ethyl formate in presence of sodium ethoxide, *ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-α-thiol-β-hydroxyacrylate*,

$$NH<\begin{matrix}C[S\cdot C(CH\cdot OH)\cdot CO_2Et]:N \\ CO\text{------------------------}CH\end{matrix}>CMe,$$

m. p. 106—108°, is produced, which forms colourless crystals; an attempt to reduce this compound with sodium amalgam resulted in the formation of 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolacetic acid. By the condensation of thiocarbamide with ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-α-thiol-β-hydroxyacrylate, *4-methyl-2(tetrahydro-2′-thio-6′-pyrimidonethiol)-1 : 6-dihydro-6-pyrimidone*,

$$CS<\begin{matrix}NH-CO \\ NH\cdot CH\end{matrix}>C\cdot SC<\begin{matrix}NH\cdot CO \\ N-CMe\end{matrix}>CH,$$

is produced, which forms clusters of prisms, and does not melt below 300°.

Diethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thioloxalylacetate,

$$NH<\begin{matrix}C[S\cdot CH(CO\cdot CO_2Et)\cdot CO_2Et]:N \\ CO\text{------------------------------}CH\end{matrix}>CMe,$$

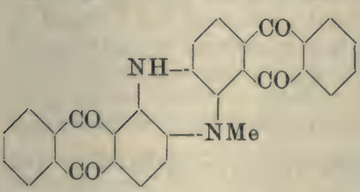
m. p. 139—140°, obtained by the action of ethyl oxalate on ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolacetate, crystallises in stout, colourless blocks; it condenses with thiocarbamide with formation of a *compound*,

$$\begin{matrix}NH\cdot CO\cdot C-S-C{=}N-CO \\ | \quad\quad\quad \| \quad\quad | \quad\quad | \\ CS\cdot NH\cdot C\cdot CO\cdot N\cdot CMe:CH\end{matrix} \text{ or } \begin{matrix}NH\cdot CO\cdot C-S-C{=}N-CMe \\ | \quad\quad\quad \| \quad\quad | \quad\quad \| \\ CS\cdot NH\cdot C\cdot CO\cdot N\cdot CO\cdot CH\end{matrix},$$

m. p. 164—165°, which crystallises in hexagonal tablets. E. G.

Preparation of Halogenated Derivatives of Indigotin. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 234961).—When 4 : 4′-dichloroindigotin is suspended in nitrobenzene (or other indifferent liquids), cooled, and treated with chlorine, further halogenation takes place, yielding tri- and tetra-chloro-derivatives. The corresponding bromo-derivatives are obtained when the substance is suspended in dilute sulphuric acid and treated with bromine at a temperature below 5°. F. M. G. M.

[Preparation of Methylindanthren.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 234294). — *Methylindanthren* (annexed formula), dark blue needles with metallic lustre, is prepared by boiling 2-bromo-1-aminoanthraquinone with 2-bromo-1-methylaminoanthraquinone in the presence of sodium acetate and cupric chloride in naphthalene solution; it dissolves with a yellowish-brown colour in concentrated sulphuric acid. F. M. G. M.



Action of Nitrous Acid on Substituted Hydrazidines. GIACOMO PONZIO and C. GASTALDI (*Gazzetta*, 1911, 41, i, 793—796).—The substituted hydrazidines previously described (compare Ponzio, Abstr., 1910, i, 443, 699) when treated with nitrous acid do not yield

tetrazoles, but, instead, the hydrogen of the imino-group is displaced by –NO, so that ω-aminobenzaldehyde-*p*-nitrophenylhydrazone,

$$NH_2\cdot CPh\colon N\cdot NH\cdot C_6H_4\cdot NO_2,$$

yields *ω-aminobenzaldehydenitroso*-p-*nitrophenylhydrazone*,

$$NH_2\cdot CPh\colon N\cdot N(NO)\cdot C_6H_4\cdot NO_2.$$

This nitroso-compound is insoluble in alkali hydroxides, and when boiled with water gives ω-aminobenzaldehyde-*p*-nitrophenylhydrazone and benzoyl-*p*-nitrophenylhydrazine, $COPh\cdot NH\cdot NH\cdot C_6H_4\cdot NO_2$.

ω-Aminobenzaldehydenitroso-*p*-nitrophenylhydrazone forms small, yellow laminæ, m. p. 127° (decomp.). It gives an emerald-green coloration with concentrated sulphuric acid and phenol. R. V. S.

Preparation of Secondary 4-Dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone Citrate. RUDOLF OTTO (D.R.-P. 234631).—Two salts of this base with citric acid have previously been described, and the "citrovanille" employed in pharmacy consists of mixtures of both in varying proportions. The primary salt (a syrup) is prepared from equal molecular proportions of the base and acid, the tertiary, containing 3 mols. of the base, has similar properties, whilst the secondary, 4-*dimethylamino*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone citrate*, $C_6H_8O_7(C_{13}H_{17}ON_3)_2$, has now been prepared by allowing the requisite proportions of the components to react either in warm aqueous solution at 75° or in a fusion without solvent; it crystallises from hot water. F. M. G. M.

Isomeride of *apo*Safranine and the Third Isomeride of Phenosafranine. FRIEDRICH KEHRMANN and JOSÉ RIERA Y PUNTI (*Ber.*, 1911, **44**, 2622—2627).—2 : 4 : 6 : 5′-*Tetranitro*-2′-*anilinodiphenylamine*, $C_6H_2(NO_2)_3\cdot NH\cdot C_6H_3(NO_2)\cdot NHPh$, brownish-yellow crystals, decomp. above 174°, obtained by warming equal molecular quantities of picryl chloride and 4-nitro-2-aminodiphenylamine in alcoholic solution, is converted in alcoholic suspension by concentrated sodium hydroxide into 1 : 3 : 7-*trinitro*-10-*phenyldihydrophenazine*, $C_6H_2(NO_2)_2{<}{}^{NH}_{NPh}{>}C_6H_3\cdot NO_2$, blackish-violet needles, decomp. above 265°, which dissolves in hot alcoholic sodium hydroxide with a violet colour. When suspended in glacial acetic acid and reduced by stannous chloride and hydrochloric acid, it is reduced to the *triaminophenyldihydrophenazine* (isolated as the yellow *stannichloride*), which loses ammonia by careful warming in faintly alcoholic solution, the subsequent addition of sodium chloride precipitating 2 : 6-*diamino*-10-*phenylphenazonium chloride*, $NH_2\cdot C_6H_3{<}{}^{N}_{NPhCl}{>}C_6H_3\cdot NH_2$. This salt forms blackish-violet, prismatic crystals with a bronze lustre, yields a violet-blue aqueous solution (so also do other mono-acidic salts), a brown solution in slightly fuming sulphuric acid, and a greenish-blue solution in concentrated sulphuric acid, which changes to magenta-red and finally to violet-blue on sufficient dilution with water; these colour changes indicate the existence of four series of salts, as is the case with phenosafranine itself. This new *iso*phenosafranine dyes tannined cotton a dirty greenish-blue, the

colour changing to red by treatment with dilute hydrochloric acid, and by washing to a blue which is fast to alkalis and soap.

*iso*Phenosafranine chloride and acetic anhydride at the ordinary temperature yield an *acetyl* derivative,

$$NH_2\cdot C_6H_3 \lessgtr \begin{matrix} N \\ NPhCl \end{matrix} > C_6H_3\cdot NHAc,$$

reddish-brown needles, from which by the elimination of the amino-group is obtained the *acetyl* derivative of *iso-apo*safranine chloride, $C_6H_4 \lessgtr \begin{matrix} N \\ NPhCl \end{matrix} > C_6H_3\cdot NHAc$; the corresponding *nitrate*, *ferrichloride*, and *platinichloride* are mentioned. iso-apo*Safranine chloride*, obtained by hydrolysing the preceding acetyl derivative, is an almost black, crystalline powder, which is unstable in solution; the *platinichloride*, $2C_{18}H_{14}N_3,PtCl_6$, is a black, crystalline powder.

*iso*Phenosafranine chloride and acetic anhydride and sodium acetate on the water-bath yield the *diacetyl* derivative,

$$NHAc\cdot C_6H_3 \lessgtr \begin{matrix} N \\ NPhCl \end{matrix} > C_6H_3\cdot NHAc,$$

brownish-red crystals with a bronze lustre; the *platinichloride* is a brownish-red, crystalline substance. C. S.

Third Isomeride of *apo*Safranine. FRIEDRICH KEHRMANN and A. MASSLENIKOFF (*Ber.*, 1911, 44, 2628—2631. Compare preceding abstract).—When the green *iso*phenosafranine chloride (1 : 3-diamino-10-phenylphenazonium chloride) undergoes prolonged treatment at the ordinary temperature with acetic anhydride and acetic acid, it is converted into 3-*amino*-1-*acetylamino*-10-*phenylphenazonium chloride*, $NHAc\cdot C_6H_2(NH_2) \lessgtr \begin{matrix} N \\ NPhCl \end{matrix} > C_6H_4$, bronze crystals (the *platinichloride*, *dichromate*, *aurichloride*, and *iodide* are described), from which 1-*amino*-10-*phenylphenazonium* salts are obtained by elimination of the amino-group and subsequent hydrolysis; the *nitrate*, *bromide*, *platinichloride*, *dichromate*, *iodide*, and *aurichloride* are described. The *acetyl* derivative, which is prepared best from the bromide, is obtained in small, chocolate-brown crystals, and forms a dark brown, crystalline *platinichloride*. C. S.

Synthesis of Naphthaphenazine Derivatives. FRIEDRICH KEHRMANN and JOSÉ RIERA Y PUNTI (*Ber.*, 1911, 44, 2618—2621).—2 : 4-*Diaminonaphthaphenazine*, $C_{10}H_6 < \begin{matrix} N \\ N \end{matrix} > C_6H_2(NH_2)_2$, obtained by reducing picryl-β-naphthylamine with the calculated amount of stannous chloride in boiling alcohol and concentrated hydrochloric acid, is purified best by means of the *diacetyl* derivative, yellow leaflets, m. p. 340° (decomp.), and forms red crystals which sublime at 320° with partial decomposition. Its diacetyl derivative does not form an azonium compound with methyl sulphate.

1 : 3-*Diaminonaphthaphenazine*, obtained in a similar manner from picryl-α-naphthylamine, forms dark red crystals and sublimes at 290—300° (decomp.). The *diacetyl* derivative, yellow needles, m. p. 320° (decomp.), easily combines with methyl sulphate in nitrobenzene

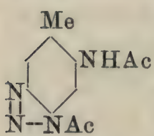
at 150°, yielding after hydrolysis with concentrated hydrochloric acid, 1 : 3-*diaminomethylnaphthaphenazonium chloride*,

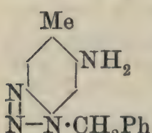
$$C_6H_2(NH_2)_2{<}{\genfrac{}{}{0pt}{}{N\text{———}}{N(MeCl)}}{>}C_{10}H_6,$$

dark red needles; the *platinichloride*, $2C_{17}H_{15}N_4,PtCl_6$, is described.

C. S.

Preparation of Iminoalkyl Derivatives of Azimino-o-toluidides. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 234966).—*Acetylaziminoaceto*-o-*toluidide* (annexed formula), m. p. 222—224°, was prepared by the reduction (iron and acetic acid) and subsequent diazotisation of 5-nitrodiacetyl-*m*-tolylenediamine; the acetyl group in the azimino-ring was then eliminated by boiling with sodium hydroxide, yielding on acidification 4:5-*azimino-2-aceto-*o-*toluidide*, a colourless powder, m. p. 235—237°; this was converted into its *benzyl* derivative, the remaining acetyl group removed by heating with sulphuric acid, and the resulting 4:5-*benzylazimino-*o-*toluidine* (annexed formula) precipitated with an alkali hydroxide; it forms a crystalline powder, m. p. 161—163°.





Other alkyl derivatives of this base can be readily prepared in a similar manner. F. M. G. M.

Diguanides. GEORG COHN (*J. pr. Chem.*, 1911, [ii], 84, 394—409).—Diguanides of the type $NH{:}C(NHR){\cdot}NH{\cdot}C(NH_2){:}NH$, where R = aryl, are readily obtained in the form of their hydrochlorides by heating dicyanodiamide with the hydrochlorides of aromatic amines in aqueous solution.

Phenyldiguanide (Lumière and Perrin, Abstr., 1905, i, 249), prepared from aniline hydrochloride and dicyanodiamide, forms a *picrate*, crystallising in yellow needles, m. p. 176—179°, with previous sintering.

m-*Nitrophenyldiguanide*, $NO_2{\cdot}C_6H_4{\cdot}C_2H_6N_5$, obtained from *m*-nitroaniline, forms amber-yellow prisms or rhombic leaflets, m. p. 147—149°; it crystallises with alcohol in transparent prisms having a colour resembling that of potassium dichromate; it forms a yellow *hydrochloride* and a *picrate*, m. p. 210—211°.

p-Hydroxyphenyldiguanide, $OH{\cdot}C_6H_4{\cdot}C_2H_6N_5$, prepared from *p*-aminophenol hydrochloride, crystallises in spherical aggregates of long, white needles, which become brown at 200° and have m. p. 211°; the hydrochloride has m. p. 203° (compare *loc. cit.*); the *picrate*, m. p. 205—206°, with previous sintering at 203°; when heated with acetic anhydride and sodium acetate, it yields a substance, m. p. 236—237°, which is considered to be an acetyl derivative of the compound $NH{:}C{<}{\genfrac{}{}{0pt}{}{NH{\cdot}C({:}NH)}{N\text{=====}CMe}}{>}N{\cdot}C_6H_4{\cdot}OH$.

p-*Phenetyldiguanide*, $OEt{\cdot}C_6H_4{\cdot}C_2H_6N_5$, crystallises in colourless leaflets, m. p. 170—172° (decomp.); the hydrochloride (Lumière and Perrin, *loc. cit.*) and *picrate*, m. p. 186—189°, are described. When dissolved in concentrated sulphuric acid and the resulting solution

treated with water, the hydrochloride yields a substance, m. p. 225—226°, to which the author assigns the formula

$$OEt\cdot C_6H_4\cdot NH\cdot CO\cdot NH\cdot C(NH_2)\colon NH.$$

Phenetyldiguanide condenses with ethyl oxalate in alcoholic solution, yielding the compound $OEt\cdot C_6H_4\cdot N{<}\begin{matrix} C(\colon NH)\cdot NH\cdot C\colon NH \\ CO\text{———}CO\cdot NH \end{matrix}$, which has m. p. 195—196° (decomp.); it forms *additive* compounds with phenols, and condensation products with formaldehyde and salicylaldehyde. When heated with acetic anhydride and sodium acetate, it yields a *diacetyl* derivative of the triazine base,

$$NH\colon C{<}\begin{matrix} NH\cdot C(\colon NH) \\ N\text{=====}CMe \end{matrix}{>}N\cdot C_6H_4\cdot OEt.$$

Ethyl phenyldiguanide-p-*carboxylate*, $C_2H_6N_5\cdot C_6N_4\cdot CO_2Et$, prepared from ethyl *p*-aminobenzoate, crystallises with one molecule of water in broad-pointed leaflets, m. p. 173°; the anhydrous compound has m. p. 177—178° (decomp.); the *hydrochloride* forms colourless leaflets or prisms; the *picrate* has m. p. 196—197°.

α-Naphthyldiguanide, $C_{12}H_{13}N_5$, forms colourless, iridescent leaflets, m. p. 154—155°, and yields a *hydrochloride* and a *picrate*, m. p. 200—203°.

m-*Phenylenebidiguanide*, $C_6H_4(C_2H_6N_5)_2$, prepared from *m*-phenylenediamine hydrochloride, has m. p. 165—167° (decomp.), and yields a *picrate*, m. p. 208—210°.

Diphenylbidiguanide, $C_{12}H_8(C_2H_6N_5)_2$, obtained from benzidine (1 mol.) and dicyanodiamide (2 mols.), has m. p. 241°; the *hydrochloride* and *sulphate* are described.

The interaction of benzidine hydrochloride and dicyanodiamide in equimolecular proportions yields 4′-*amino*-4-*diphenylyldiguanide*,

$$NH_2\cdot C_6H_4\cdot C_6H_4\cdot C_2H_6N_5,$$

which has m. p. 203—204°, and reacts with nitrous acid to form a diazonium compound which couples with α-naphthol, yielding a purple-red *azo*-dye; the *azo*-dyes obtained from β-naphthol, resorcinol, phenol, salicylic acid, and phenylmethylpyrazolone are also mentioned.

Phenyldiguanide-o-*carboxylic anhydride*,

$$C_6H_4{<}\begin{matrix} NH\cdot C\colon NH \\ CO-N\cdot C(NH_2)\colon NH \end{matrix},$$

prepared from anthranilic acid, is a crystalline powder, m. p. above 280°, and forms a sparingly soluble *hydrochloride*.

Phenylmethyldiguanide, $NMePh\cdot C_2H_5N_4$, obtained from methylaniline, crystallises in hygroscopic needles, which decompose when heated.

The interaction of phenylhydrazine hydrochloride and dicyanodiamide yields phenylguanazole (Pellizari, Abstr., 1892, 356), of which the *hydrochloride* and *picrate*, m. p. 225°, are mentioned.

Many of the diguanides described above give characteristic precipitates with potassium ferrocyanide, ammonium molybdate, and with nickel and cobalt salts.

Quantitative experiments on the precipitation of a large number of dyes by means of the diguanide hydrochlorides are also described.

F. B.

Distribution of Auxochromes in Azo-compounds. HUGO KAUFFMANN and W. KUGEL (*Ber.*, 1911, 44, 2386—2389).—For the study of the effect of the distribution of the auxochromes in azo-compounds (compare Kauffmann and Franck, Abstr., 1906, i, 841), the compounds of the type $N_2[C_6H_3(OMe)_2]_2$, derived from quinol, resorcinol, and catechol, have been compared. These are coloured very differently; the quinol derivative is dark red, that from resorcinol is orange-red or orange, and the catechol derivative is orange-yellow. The rules as to the effect of the positions of the auxochromes therefore apply to azo-compounds. In hydrochloric acid solution the quinol derivative gives a blue, the resorcinol a red, and the catechol a carmine-red coloration.

Resorcinol benzoate couples with diazotised aniline to form p-*benzeneazoresorcinol monobenzoate*, which forms yellow crystals, m. p. 180°, and is hydrolysed to benzeneazoresorcinol, m. p. 169°.

By reduction of nitroresorcinol dimethyl ether with tin and hydrochloric acid, the *hydrochloride* of *aminoresorcinol dimethyl ether* is obtained in long, bluish-white needles. When diazotised, it couples with resorcinol to form 2 : 4-*dimethoxybenzeneazoresorcinol*,

$$C_6H_3(OH)_2\cdot N_2\cdot C_6H_3(OMe)_2,$$

which forms almost black crystals with a green reflex, and is soluble in sodium hydroxide with an orange-yellow coloration, m. p. 186°. Strong hydrochloric acid dissolves it with a dark red, sulphuric acid with a dark blue, coloration.

2 : 4 : 2′ : 4-*Tetramethoxyazobenzene*, $N_2[C_6H_3(OMe)_2]_2$, formed by methylation of the above substance with methyl sulphate, separates in red crystals, m. p. 181°.

3 : 4 : 3′ : 4′-*Tetramethoxyazobenzene* prepared by reduction of nitroveratrole, forms yellow crystals, m. p. 163°.

2 : 5 : 2′ : 5′-Tetramethoxyazobenzene (compare Baessler, Abstr., 1884, 1329) forms dark red crystals, m. p. 142°, soluble in concentrated sulphuric acid with a violet-red, and in hydrochloric acid with a blue, coloration. E. F. A.

Action of Sodium Sulphite and of Sodium Hydrogen Sulphite on Some Azo-dyes. ROBERTO LEPETIT and E. LEVI (*Gazzetta*, 1911, 41, i, 675—688. Compare Abstr., 1909, i, 569; Nietzki and Helbach, Abstr., 1897, i, 226).—From the reaction between sodium sulphite and nitrobenzeneazosalicylic acid (alizarin-yellow-R) the following substances were isolated: (1) *p*-aminobenzeneazosalicylic acid; (2) *p*-nitroaniline; (3) ammonia; (4) an aminosulphosalicylic acid, to which the formula

$$OH\cdot C_6H_2(NH_2)(CO_2H)\cdot SO_3H,H_2O$$

is ascribed. The last-named substance crystallises in colourless, silky needles (and also in small, compact cubes), which dissolve in alcohol, giving a green, intensely fluorescent solution. The aqueous solution gives a cherry-red coloration with ferric chloride, and reduces ammoniacal silver solutions. Preparation of the substance by sulphonation of aminosalicylic acid shows that the substance is identical with that obtained by Mandt (*Ber.*, 1877, 10, 1701). It was

not possible to obtain salts with the heavy metals, but the arsenate crystallises in red needles. An acetyl derivative was obtained in the form of its sodium salt, which crystallises with $1H_2O$. The barium salt also contains $1H_2O$, but is not crystalline.

The action of sodium hydrogen sulphite is more vigorous than that of sodium sulphite, so that, working under the same conditions (in boiling water), after one hour most of the dye is decomposed into *p*-nitroaniline and aminosulphosalicylic acid without formation of aminobenzeneazosalicylic acid.

The reaction between sodium hydrogen sulphite and *p*-aminobenzeneazosalicylic acid (in an autoclave at 130°) proceeds similarly to that just described.

Benzeneazosalicylic acid and sodium sulphite yield (1) a *substance*, which crystallises in small, brown needles, m. p. 140°, which is possibly the hydrazo-compound, $NHPh\cdot N(SO_3H)\cdot C_6H_3(OH)\cdot CO_2H$; (2) aminosulphosalicylic acid.

Benzeneazosalicylic acid is more readily acted on by sodium hydrogen sulphite with formation of the following products: (1) aniline; (2) aminosulphosalicylic acid; (3) a substance which could not be isolated; (4) an *amino*-compound, m. p. 170—173°, which is a benzidine derivative; (5) a *compound*, m. p. 126—128°, which contains sulphur but no nitrogen.

Sodium hydrogen sulphite reacts with diphenylbisazosalicylic acid (chrysamin-G) much less readily than with the preceding compounds. The products isolated were benzidine sulphate and aminosulphosalicylic acid. R. V. S.

Aromatic Nitro-derivatives. II. ROBERTO CIUSA (*Gazzetta*, 1911, 41, i, 688—697. Compare Abstr., 1907, i, 874).—The present paper deals with the action of picryl chloride on *cyclo*hexanoneazine and on benzaldoxime, and the preparation of *cyclo*hexanonemono- and di-nitrophenylhydrazones is described. The author also finds that trinitro-ψ-cumene is strongly dissociated in formic acid solution, so that a mobile atom of hydrogen is not a necessary condition for the dissociability of aromatic polynitro-derivatives. It is suggested that the power of dissociation depends on the presence either of a free hydrogen atom in the nucleus or of a halogen or nitro-group in the ortho-position with respect to another nitro-group.

2 : 4 : 6 : 4′-Tetranitrohydrazobenzene gives a *potassium* salt, $C_{12}H_6O_8N_6K_2$, which crystallises in small, dark needles with a violet sheen.

2 : 4 : 6 : 4′-Tetranitrohydrazobenzene when heated with concentrated nitric acid yields 2 : 4 : 6 : 4′-*tetranitroazobenzene*,

$$C_6H_2(NO_2)_3N:N\cdot C_6H_4\cdot NO_2,$$

which forms orange-red needles, m. p. 163—164°. It dissolves in alkalis with difficulty, giving a red coloration.

cyclo*Hexanoneazine* (from *cyclo*hexanone and hydrazine hydrate) has b. p. 165°/25 mm., m. p. 35°. On treatment with picryl chloride, it yields cyclo*hexanonetrinitrophenylhydrazone*, $C_6H_{10}:N\cdot NH\cdot C_6H_2(NO_2)_3$, which crystallises in flat, red needles, m. p. 133°, and dissolves in alkali, giving a reddish-brown coloration. cyclo*Hexanone*-2 : 4-*dinitro*-

phenylhydrazone, $C_6H_{10}\colon N\cdot NH\cdot C_6H_3(NO_2)_2$, forms golden-yellow scales, m. p. 145°. cyclo*Hexanone*-p-*nitrophenylhydrazone*,

$$C_6H_{10}\colon N\cdot NH\cdot C_6H_4\cdot NO_2,$$

crystallises in yellowish-brown needles, m. p. 146°; it is insoluble in water, and may be used to detect *cyclo*hexanone in water.

When α-benzaldoxime is heated with picryl chloride in alcoholic solution for two hours, picramide is obtained.

A nitro-group is eliminated from trinitro-ψ-cumene when treated with alkali, and a *potassium* salt, $C_6Me_3(NO_2)_2\cdot OK$, can be obtained. By the action of dilute hydrochloric acid, this salt is converted into a yellow *substance*. R. V. S.

Hydrazo-compounds. VII. Methylhydrazotoluene, Methyltolidine, and Ethylbenzidine. BERTHOLD RASSOW and ARNO BECKER (*J. pr. Chem.*, 1911, [ii], 84, 329—351. Compare this vol., i, 820, 821).—N-*Methylhydrazo-o-toluene*, $C_6H_4Me\cdot NH\cdot NMe\cdot C_6H_4Me$, is prepared by heating a benzene solution of hydrazo-*o*-toluene with excess of methyl sulphate and magnesium oxide for thirty-six to forty hours in an atmosphere of carbon dioxide; it crystallises in rhombic, rectangular, or almost square plates, m. p. 84°.

N-*Methyl*-o-*tolidine*, $NHMe\cdot C_6H_3Me\cdot C_6H_3Me\cdot NH_2$, obtained in the form of its *hydrochloride*, $C_{15}H_{18}N_2,2HCl$ (decomp. 260—280°), by the addition of concentrated hydrochloric acid to an alcoholic solution of the preceding compound, has m. p. 85°; it yields an unstable, yellowish-brown *platinichloride*, $C_{15}H_{18}N_2,H_2PtCl_6$, a *picrate*, crystallising in yellow, microscopic needles, which decompose at 184—186°, and a *dibenzoyl* derivative, $NHBz\cdot C_6H_3Me\cdot C_6H_3Me\cdot NMeBz$, m. p. 156°; when heated with salicylaldehyde in alcoholic solution, it forms a *salicylidene* derivative, $NHMe\cdot C_6H_3Me\cdot C_6H_3Me\cdot N\colon CH\cdot C_6H_4\cdot OH$, which crystallises in needles, m. p. 120°. It reacts with one or two mols. of nitrous acid, yielding (I) 4-*methylamino*-3 : 3'-*dimethyldiphenyl*-4'-*diazonium chloride*, $NHMe\cdot C_6H_3Me\cdot C_6H_3Me\cdot N_2Cl$, and (II) 4-*methylnitrosoamino*-3 : 3'-*dimethyldiphenyl*-4'-*diazonium chloride*,

$$NO\cdot NMe\cdot C_6H_3Me\cdot C_6H_3Me\cdot N_2Cl.$$

4-*Methylamino*-3 : 3'-*dimethyldiphenyl*-4'-*azo*-β-*naphthol*,

$$NHMe\cdot C_6H_3Me\cdot C_6H_3Me\cdot N\colon N\cdot C_{10}H_6\cdot OH,$$

prepared by coupling the diazonium compound (I) with β-naphthol, forms lustrous, dark red crystals, which have m. p. 90—92° and decompose at 120°.

4-*Methylnitrosoamino*-3 : 3'-*dimethyldiphenyl*-4'-*azo*-β-*naphthol*,

$$C_{20}H_{22}O_2N_4,$$

prepared from (II) and β-naphthol, has m. p. 173°, and is converted into the preceding compound when heated with alcoholic hydrogen chloride.

4-*Methylamino*-3 : 3'-*dimethyldiphenyl*-4'-*azo*-p-*dimethylaniline*,

$$NHMe\cdot C_6H_3Me\cdot C_6H_3Me\cdot N\colon N\cdot C_6H_4\cdot NMe_2,$$

begins to decompose at 100°, and yields a dark red *hydrochloride*; the *nitroso*-derivative, prepared from (II) and dimethylaniline, forms reddish-yellow, triclinic prisms, which have m. p. 160° and decompose at 180°. It combines with benzenediazonium chloride, yielding 5-*benzeneazo*-4-*methylamino*-3 : 3'-*dimethyldiphenyl*-4'-*azo*-p-*dimethylaniline*,

$NPh:N\cdot C_6H_2Me(NHMe)\cdot C_6H_3Me\cdot N:N\cdot C_6H_4\cdot NMe_2$, which decomposes at 180—190°.

Sodium 4-*methylamino*-3 : 3′-*dimethyldiphenyl*-4′-*azo*-β-*naphthol*-(3 : 6)-*disulphonate*, $C_{25}H_{21}O_7S_2Na_2$, prepared from the diazonium compound (I) and R-salt, has no definite m. p., and couples with benzenediazonium chloride, yielding *sodium* 5-*benzeneazo*-4-*methylamino*-3 : 3′-*dimethyldiphenyl*-4′-*azo*-β-*naphthol*-(3 : 6)-*disulphonate*,

$$NPh:N\cdot C_6H_2Me(NHMe)\cdot C_6H_3Me\cdot N:N\cdot C_{10}H_4(SO_3Na)_2\cdot OH,$$

which is dark red and dyes cotton reddish-violet; with diazotised sulphanilic acid it forms a deep bluish-violet *bisazo-dye*.

N-*Ethylbenzidine* $NH_2\cdot C_6H_4\cdot C_6H_4\cdot NHEt$, obtained by heating a benzene solution of hydrazobenzene with ethyl sulphate in the presence of magnesium oxide, crystallises in leaflets or needles, m. p. 73—74°. F. B.

Electrochemistry of Proteins. VII. The Mode of Formation and Ionisation of the Compounds of Proteins with Inorganic Acids and Bases. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1911, 15, 521—550. Compare this vol., ii, 460).—The author propounds the hypothesis that the combining power of protein for acids and bases resides elsewhere than in the terminal NH_2 and CO_2H groups of the protein chain. The typical group $-CO\cdot NH-$ (alternatively $-C(OH):N-$) is held to be the seat of the amphoteric properties. The main arguments are as follows.

The soluble neutral hydrochloride of edestin contains nine times as much acid as the insoluble hydrochloride. Hence there must be nine or a multiple of nine basic centres in the edestin molecule. On a probable molecular weight of 7000, nine NH_2 groups correspond with more than 10% of the total nitrogen. In caseinogen the maximum combining capacity for alkali is sixteen times the minimum amount required to render the caseinogen soluble. On a probable molecular weight of 17,600 this requires 12½% of the total oxygen to be in the terminal CO_2H groups. Similar calculations made for egg-albumin also lead to percentages which are too high to be consistent with the catenary structure of the protein molecule.

The non-hydrolysable character of the protein salts is presumptive evidence that they are not ordinary amino-salts or carboxylates in the formation of which water is split off. The anions and cations of caseinogen and ovimucoid salts are protein ions, and the dissociation of potassium caseinogenate is not diminished by potassium chloride.

Burgarski and Liebermann showed (Abstr., 1898, i, 716), by potentiometric methods, that as many chlorine as hydrogen ions are removed from circulation when egg-albumin is dissolved in dilute hydrochloric acid. A mixture of ovimucoid hydrochloride with potassium caseinogenate has at first a conductivity equal to the sum of the conductivities of the constituent solutions, and only very slowly deposits caseinogen as a result of the formation of potassium chloride, since the inorganic constituents of the protein salts are combined in a non-dissociable form.

From analysis of the anodic and cathodic solutions after electrolysis of potassium caseinogenate, the loss of caseinogen from the anodal

region, is about double the loss from the cathodal region. This is in harmony with the assumption that the positive and negative ions of caseinogen are of about equal mass and mobility. The formula of protein being written $R^1C(OH){:}NR^2$, the ionised salts may be written $R^1C(ONa)^{\cdot\cdot} + HN(OH'')R_2$ and $R^1C(OH)^{\cdot\cdot} + HNCl''R^2$ respectively. The ions are assumed to be bivalent from the electrochemical equivalents.

Kossel has drawn attention to the fact that the combining capacity of a protein for acids is proportional to the diamino-acid content, and the combining capacity for bases is proportional to the dicarboxylic acid content. Hence it is probable that the $-C(OH){:}N-$ groups function only when in contiguous pairs. This leads to the formulæ: $R^1{<}\begin{matrix}C(OK)^{\cdot\cdot} + NH(OH'')R^2 \\ C(OK)^{\cdot\cdot} + NH(OH'')R^3\end{matrix}$ and $\begin{matrix}R^1C(OH)^{\cdot\cdot} + NHCl'' \\ R^2C(OH)^{\cdot\cdot} + NHCl''\end{matrix}{>}R^3$ for the potassium salt and the hydrochloride of protein respectively.

These formulæ are in agreement with the conductivity and freezing-point determinations in the case of ovimucoid dihydrochloride. Ovimucoid monohydrochloride is supposed to be

$$\begin{matrix}R^1C(OH)^{\cdot\cdot} + HNCl''— \\ R^2C(OH)^{\cdot\cdot} + HN(OH)''\end{matrix}{>}R^3.$$

R. J. C.

Precipitation of Protein by Zinc Sulphate. FRITZ LIPPICH (*Zeitsch. physiol. Chem.*, 1911, 74, 360—391).—A detailed discussion of the literature leads to the conclusion that the adsorption hypothesis does not explain adequately the formation of metallic albuminates; it is undesirable to extend to proteins the conclusions based on experiments made with inorganic colloidal material.

In a series of experiments the proteins of horse-serum were precipitated by increasing quantities of zinc sulphate, and the amount of protein and zinc salt remaining in the filtrate determined, whence the composition of the precipitate could be calculated. It is found that, under certain conditions, the amount of zinc in the precipitate is independent of the concentration of the protein, and also of the initial concentration of the zinc salt. The power of protein to form a zinc salt increases on dilution, but a maximum is soon reached. The results are not in agreement with the adsorption theory, and the change is better represented as a chemical interaction between an amphoteric and a non-amphoteric electrolyte leading to an equilibrium: $ZnSO_4 + 2Na$ protein $\rightleftharpoons Na_2SO_4 + Zn(\text{protein})_2$. The left-hand side of the equation preponderates so long as protein is present in excess, but the amount of precipitate increases on standing, and especially on dilution. When the amount of metallic salt is increased, a point is reached when a sparingly soluble substance is formed, and the reaction is almost entirely in the sense of the equation from left to right. A still further increase in concentration of the metallic salt causes reaction in the opposite direction, and the precipitate will begin to dissolve. For the full discussion of the results the original should be consulted. E. F. A.

What is the Cause of the Separation of Albumin in Bottled Beer which has been Subjected to Normal Treatment in Brewery and Cellar? FRITZ EMSLANDER (*Koll. Chem. Beihefte*, 1911, 3, 47—84).—The conditions favourable to the separation of albumin are discussed with reference to the literature on the subject, and the conclusion is reached that the process is determined primarily by electrochemical effects resulting from the presence of electrolytes. These bring about chemical change in the molecules of albumin, and the transformation is accompanied by alterations in the surface-tension and potential difference between the colloidal particles and the aqueous medium. Coagulation results, and this leads ultimately to turbidity and the deposition of solid substances. H. M. D.

The Hydrolytic Action of Hydrogen Peroxide. CARL NEUBERG and SOICHIRO MIURA (*Biochem. Zeitsch.*, 1911, 36, 37—43).—Hydrogen peroxide in the presence of a manganese or iron salt will bring about at the ordinary temperature the hydrolysis of a number of compounds of high molecular weight. Egg-albumin after treatment yields 10% of its nitrogen as ammonia when heated with magnesia. Substances of an aldehydic and ketonic nature are also formed. Gelatin under similar conditions gives 10·4% of its nitrogen as amide-nitrogen.

Starch, soluble starch, and glycogen are hydrolysed with formation of reducing and fermentable sugars, which yield mixed phenylosazones. Phenylglucosazone is obtained from the products from soluble starch, and phenylmaltosazone from those from glycogen. Inulin gives lævulose.

Yeast nucleic acid gives 23·2% of its nitrogen as amide-nitrogen, and phosphoric acid is set free. With sodium chondroitin sulphate, sulphuric acid is liberated, whilst lecithin yields fatty acids. W. J. Y.

The Reactions between Ferments and Anti-ferments. MARTIN JACOBY (*Biochem. Zeitsch.*, 1911, 34, 485—494. Compare Abstr., 1907, i, 811; ii, 108; 1908, i, 236; ii, 743).—Previous observations that the combination between rennet and anti-rennet of serum is destroyed by acid is confirmed. If acid is allowed to act on serum for some time, the anti-rennet is destroyed. Neither the ferment, anti-ferment, nor the combination are soluble in ether. If rennet solution is shaken, its fermentative action is diminished, and can be neutralised by a smaller quantity of serum. S. B. S.

Action of Oxydases. I. REGINALD O. HERZOG and A. POLOTZKY (*Zeitsch. physiol. Chem.*, 1911, 73, 247—257. Compare Engler and Herzog, Abstr., 1909, ii, 495).—The peroxydase was prepared from sugar beet, and its action in presence of hydrogen peroxide tested on the leuco-base of brilliant-green, on a mixture of *p*-phenylenediamine and dimethylaniline, and on vanillin. Dyes are formed in the first two cases, and a precipitate in the last. The optimum reaction is shown to depend on the concentration of each of the three reacting substances. The change in the case of brilliant-green can be followed colorimetrically. In addition to the formation of colour there is a

bleaching action also brought about by the oxydase. Complete bleaching takes place when the proportion of leuco-base is small compared with that of hydrogen peroxide, provided an excess of enzyme is present. The formation of the dye is much more rapid than the bleaching.

The three possible combinations of mixtures of two of the three reacting substances were prepared and set aside for fourteen hours before the third substance was added. The mixture leuco-base + peroxide reacts the most quickly, that of peroxydase + peroxide is slower, whilst peroxydase + leuco-base shows a marked induction period, and the rate of dye formation is slow. The velocity of the bleaching reaction is much the same for the first and third mixtures, but less for the second. The long induction period indicates that chemical changes, in particular, the formation of additive products, must take place between the components before the formation of colour begins. The experiments indicate that a compound of leuco-base and peroxydase is formed, and that the addition of peroxide displaces the leuco-base and forms a true oxydase from the peroxydase and peroxide. Formation of dye does not take place until the concentration of the active oxydase is sufficient. E. F. A.

Action of Oxydases. II. Reginald O. Herzog and A. Meier (*Zeitsch. physiol. Chem.*, 1911, **73**, 258—265. Compare preceding abstract).—The oxydase extracted from horse-radish was tested against vanillin in presence of hydrogen peroxide, and the amount of dehydrodivanillin formed was weighed. Experiments were made with varying proportions of enzyme and hydrogen peroxide. The filtrate was tested in each case with fresh oxydase solution, and with hydrogen peroxide and guaiacum in order to test whether active peroxydase still remained. The enzyme is destroyed when the relative concentration of hydrogen peroxide is too large; when this is small, the amount of change is approximately proportional to the amount of peroxydase added. The amount of change depends on the proportions of each of the three reacting substances, and the phenomena differ from typical catalysis. The action of peroxydase is classed with the so-called induced reactions. E. F. A.

The Peroxydase of Milk. W. Grimmer (*Milchw. Zentr.*, 1911, **7**, 395—402).—The peroxydase reaction of fresh milk is shown to be due, not to the presence of inorganic catalysts, but to that of a substance closely connected with the lactalbumin. This is indicated by the similar behaviour of milk-peroxydase and lactalbumin towards precipitating agents and solvents, and, further, by the fact that all compounds which tend to denaturise lactalbumin, such as alcohols, acetone, ether, chloroform, and concentrated acids and alkalis, also lead to the destruction of the enzyme. Putrefaction has the same effect. It is suggested that the enzyme produced in the cells of the mammary gland, and liberated by the destruction of these, is either a protein possessing physical and chemical properties similar to those of lactalbumin, or that it becomes adsorbed by the latter and cannot be separated by ordinary means. H. B. H.

Organic Chemistry.

Catalytic Reactions at High Temperatures and Pressures. XXII. Decomposition of Hexane and *cyclo*Hexane; Isomerisation of *cyclo*Hexane. WLADIMIR N. IPATIEFF and N. DOWGELEWITSCH (*Ber.*, 1911, 44, 2987—2992).—At ordinary pressures, hexane and *cyclo*hexane are decomposed when passed through an iron tube at 650—700°, the decomposition being accelerated by the presence of alumina; hexane decomposes more readily than *cyclo*hexane. The gases thereby produced consist of saturated hydrocarbons, hydrogen, ethylene, propylene, and probably *iso*butylene, whilst the liquid polymerisation product contains a very small proportion of unsaturated hydrocarbons. No hydrocarbons were obtained which reacted with a nitrating mixture or with permanganate.

The course of reaction is quite different under high pressures, taking place at a much lower temperature. With hexane, at 510°, the increase in pressure takes place so rapidly that an explosion occurs, so that *cyclo*hexane only was used in these experiments. It was heated for four hours at 500—510° in the presence of alumina, at a pressure of 110—120 atmospheres; no reaction takes place at this temperature in the absence of alumina. After removal of the ethylene hydrocarbons from the liquid polymerisation product by means of sulphuric acid, the remaining liquid was divided into eleven fractions, none of which decolorised permanganate. The first three fractions, 45—80°, contained polymethylene hydrocarbons, among which was methyl *cyclo*pentane, but no saturated hydrocarbons. The fractions VI—XI, 125—280°, reacted with a nitrating mixture, and therefore contained benzene hydrocarbons; nitro-compounds were also obtained from fractions VI (125—150°) and VII (150—170°). The higher fractions contain polynuclear hydrocarbons as well as saturated hydrocarbons.

Methyl*cyclo*pentane was isolated by refractionation of the first three fractions, and identified by its physical properties and transformation into the nitro-compound. During its formation from *cyclo*hexane there is also the possibility of hexylene being formed, and this compound was also identified. This isomerisation of *cyclo*hexane takes place only at high pressures and in the presence of alumina; at ordinary pressures, even at 760°, no methyl*cyclo*pentane could be found in the products of decomposition. T. S. P.

Polymerisation of Ethylene Hydrocarbons at High Temperatures and Pressures. WLADIMIR N. IPATIEFF (*Ber.*, 1911, 44, 2978—2987).—Both ethylene and *iso*butylene when heated in an iron tube under a pressure of about 70 atmospheres (compare Abstr., 1907, i, 5) undergo rapid polymerisation at 380—400°. The liquid polymerisation products thus obtained consist of mixtures of saturated, ethylenic, and polymethylene hydrocarbons. The fractions boiling below 100° consist chiefly of the saturated and ethylene hydrocarbons, whilst the

polymethylene compounds are found chiefly in the higher-boiling fractions, the proportion being the greater the higher the boiling point. This holds, however, only for fractions boiling below 250°; above that temperature hydrocarbons are obtained which are poorer in hydrogen than the polymethylene compounds.

The following compounds were identified in the polymerisation product obtained from ethylene: *iso*pentane, hexane, heptane, octane, nonane, amylene, hexylene, nonanaphthene, α-and β-decanaphthene, hendeca-, dodeca-, tetradeca- and pentadeca-naphthenes. In the case of *iso*butylene the polymerisation product also contained some hydrocarbons which reacted with a nitrating mixture and with potassium permanganate, and were insoluble in sulphuric acid (D 1·84).

In the presence of alumina the polymerisation of ethylene gives similar results to those obtained in its absence.

At atmospheric pressure ethylene does not polymerise, even at 600°.

The ethylene hydrocarbons are probably produced by the polymerisation of ethylene itself, or from the polymethylenes by fission of the ring (compare preceding abstract). The saturated hydrocarbons are formed either by the hydrogenisation of the closed-chain hydrocarbons with fission of the ring, or else by fission of the side-chains from the polymethylene nucleus. T. S. P.

Preparation of Sulphurous Acid Derivatives of Unsaturated Hydrocarbons. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 236386).—When the unsaturated hydrocarbons of general formula $CR_2\colon CR\cdot CR\colon CR_2$ (where R is hydrogen, alkyl, or aryl groups) are treated with sulphurous acid, they yield colourless compounds, which when containing a small amount of sulphurous acid are fairly soluble in water, but an increase of the amount renders them insoluble.

When $\beta\gamma$-dimethyl-$\Delta^{\alpha\gamma}$-butadiene is saturated with sulphur dioxide in aqueous solution, it stiffens to a colourless substance somewhat resembling meerschaum; if shaken for some time with excess of sulphurous acid, an insoluble compound is formed, but if the shaking is interrupted at the right time and the solution carefully evaporated, a *compound* of $\beta\gamma$-dimethylbutadiene with sulphurous acid separates in long needles. The *compound*, prepared from isoprene and sulphurous acid, separates in colourless flakes. F. M. G. M.

α-Iodo-Δ^{δ}-hexene. JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1911, 44, 3062—3065).—The magnesium compound of α-bromo-Δ^{δ}-hexene, $CHMe\colon CH\cdot[CH_2]_3\cdot MgBr$, obtained by the action of magnesium on $\alpha\delta\epsilon$-tribromohexane (Braun and Sobecki, this vol., i, 413), is converted by the action of iodine into *α-iodo-Δ^{δ}-hexene*, $CHMe\colon CH\cdot[CH_2]_2\cdot CH_2I$. This is an almost colourless liquid, b. p. 70—75°/33 mm., and combines with trimethylamine in alcoholic solution, yielding *Δ^{δ}-hexenyltrimethylammonium iodide*, $C_6H_{11}\cdot NMe_3I$, m. p. 110°, which is extremely hygroscopic, and at once forms a yellow oil on exposure to air.

By the exhaustive methylation of α-pipecoline, Merling (Abstr., 1891, 1506) obtained a base, $C_6H_{11}\cdot NMe_2$, which forms a methiodide isomeric with the above compound, and, accordingly, must have the constitution $CH_2\colon CH\cdot[CH_2]_4\cdot NMe_2$. F. B.

Specific Gravity of Absolute Ethyl Alcohol at 25°. ANTON KAILAN (*Ber.*, 1911, 44, 2881—2884).—The author finds the density of absolute ethyl alcohol, prepared by distillation of 99·8% alcohol over calcium, to be D_4^{25} 0·78513, which agrees with Winkler's value, 0·78509 (Abstr., 1905, i, 850), within the error of experiment. This necessitates a correction in the water-content of the alcohol used by him in his measurements of the velocity of esterification of organic acids (compare Abstr., 1908, ii, 27, 28, 936), since his previous results were based on Mendeléeff's values for the density of alcohol.

Redeterminations of the velocity of esterification of benzoic acid with hydrogen chloride as catalyst give results in agreement with those obtained by Goldschmidt for alcohol distilled over calcium (Abstr., 1907, ii, 852).

The water-content of alcohol can be determined more accurately by measurement of the density than by measurement of the velocity of esterification, as recommended by Goldschmidt, even when it is less than 0·1%. T. S. P.

Use of Liquid Ammonia in Chemical Reactions. Alkyloxides. E. CHABLAY (*Compt. rend.*, 1911, 153, 819—821. Compare Doby, Abstr., 1903, i, 546; Perkin and Pratt, Trans., 1909, 95, 159).—The preparation of the alkyloxides of alkali earth metals has been realised by bringing about double decomposition between a sodium alkyloxide and the metallic nitrate in liquid ammonia solution. The resulting sodium nitrate, being soluble in the ammonia, can be separated from the alkyloxide. A second method consists in allowing an alcohol to act on a solution of calcium in liquid ammonia, when the action follows the course $2ROH + Ca(NH_3)_4 = Ca(OR)_2 + 4NH_3 + H_2$. A number of barium and strontium alkyloxides have also been prepared in this way. W. O. W.

Catalytic Dehydration of *sec.*- and *tert.*-Pinacolyl Alcohols. FRANÇOIS COUTURIER (*Bull. Soc. chim.*, 1911, [iv], 9, 898—901).—When these alcohols are dehydrated by Sabatier and Senderens' method, using the apparatus designed by Bouveault (Abstr., 1908, i, 117), the secondary alcohol (methyl*tert.*-butylcarbinol),

$$CMe_3{\cdot}CHMe{\cdot}OH,$$

gives rise to pinacolin, whilst the tertiary alcohol, dimethyl*iso*propylcarbinol, forms $\beta\gamma$-dimethyl-Δ^{α}-butylene with a small amount of $\beta\gamma$-dimethyl-Δ^{β}-butylene (compare Henry, Abstr., 1907, i, 374; 1909, i, 79, and Delacre, Abstr., 1906, i, 921; 1907, i, 459). These results support Delacre's view that *sec.*-pinacolyl alcohol is not readily isomerised, and are in opposition to Henry's results (*loc. cit.*), which indicate that the haloid esters of this alcohol undergo isomerisation when heated (Abstr., 1908, i, 881). T. A. H.

Accessory Products in the Hydrolysis of (I.) Crude Pinacone; (II.) Pure Pinacone. MAURICE DELACRE (*Bull. Soc. chim.*, 1911, [iv], 9, 885—889, 889—898).—A detailed revision of the work done by Couturier (Abstr., 1893, i, 244) and by Richard and Langlais (Abstr., 1910, i, 462) on the identification of the by-products formed in the preparation of pinacolin from pinacone.

From 10·3 kilograms of residues from the preparation of pinacolin from crude pinacone, 6·277 kilograms of material boiling at 200—220° were obtained, the remainder, after allowing 2·27 kilograms for residue and loss, being divided into eleven fractions boiling between 140° and 200°. From the portion b. p. 200—220°, two fractions, b. p. 213—214·5° and 214·5—218°, were isolated. The first of these had approximately the composition $C_9H_{14}O$, and gave an oxime, m. p. 161°, and a semicarbazone, m. p. 187°. A portion of this fraction boiling at 214°, on the contrary, gave with hydroxylamine two substances, of m. p. 60° and 88° respectively. The fraction is therefore a mixture, and it is impossible at present to say whether it contains *iso*phorone and deoxymesitylic oxide (Harries and Hubner, Abstr., 1897, i, 549). In the low boiling portion of the residues, di*iso*propenyl (Abstr., 1896, i, 591) and a hydrocarbon, C_7H_{14}, b. p. 60—63°, were found.

In the second paper details are given of a still more exhaustive fractionation of by-products from the preparation of pinacolin from crude pinacone. No mesitylene could be detected, but a substance, $C_9H_{14}O$, b. p. 210° (approx.), giving an oxime, m. p. 75°, and a semicarbazone, m. p. 196°, was obtained; this may be *iso*phorone or a new isomeride of this substance. A similar examination of the by-products resulting from the preparation of pinacolin from pure pinacone gave analogous results. T. A. H.

Autoxidation of Aliphatic Amino- and Polyhydroxy-derivatives. II. WILHELM TRAUBE (*Ber.*, 1911, **44**, 3141—3145. Compare Abstr., 1910, i, 294).—Cuprammonium oxide and the complex copper salts of aliphatic amino- and hydroxy-compounds are autoxidisable. The experiments with the latter have now been made with barium hydroxide instead of sodium hydroxide, the alkali being saturated with cupric hydroxide and oxidation effected at about 70°. Under these conditions carbon dioxide is formed in considerable quantity, and oxalic acid appears as well as formic acid.

Glycerol is oxidised to the extent of about 20% to carbon dioxide and oxalic acid, $C_3H_8O_3 + O_6 = C_2H_2O_4 + CO_2 + 3H_2O$, and about 80% to formic and oxalic acids, $C_3H_8O_3 + O_5 = C_2H_2O_4 + H_2CO_2 + 2H_2O$.

The oxidation of glyceric acid, barium gluconate, glycollic acid, glycine, and lactic acid has been studied in like manner.

E. F. A.

αβδ-Trihydroxybutane; its Conversion into Furan Derivatives and Erythritol. HENRI PARISELLE (*Ann. Chim. Phys.*, 1911, [viii], **24**, 315—410).—This paper gives a detailed, connected account of results already published (Abstr., 1908, i, 496; 1909, i, 282, 691; 1910, i, 353, 463), adding new data regarding certain of the substances described, and giving comparisons of allylcarbinol with allyl alcohol, and of αβδ-trihydroxybutane with αβγ-trihydroxybutane and glycerol.

Allylcarbinol, D^{17} 0·848, n_D^{17} 1·421, prepared as described already (Abstr., 1909, i, 282), on treatment with phosphorus tribromide or hydrogen bromide furnishes some αγ-dibromobutane along with a poor yield of the corresponding *bromide* [*bromo-Δ^α-butylene*],

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2Br,$$

D^0 1·355, D^{17} 1·33, n_D^{17} 1·465, b. p. 97—99°/760 mm., which on treatment

with solid potassium hydroxide gives $\Delta^{\alpha\gamma}$-butadiene, $CH_2:CH\cdot CH:CH_2$, identified by conversion into tetrabromobutane, m. p. 117—118° (see below). The acetate has D^0 0·93, D^{15} 0·918, n_D^{15} 1·411, and readily combines with bromine to form $\gamma\delta$-dibromobutyl acetate, D^{18} 1·73, n_D^{18} 1·508, b. p. 135°/16 mm. (compare Wagner, Abstr., 1894, i, 563). Butylcarbinol formal, $CH_2(O\cdot CH_2\cdot CH_2\cdot CH:CH_2)_2$, has D^0 0·897, D^{14} 0·88, n_D^{14} 1·4333 (Abstr., 1909, i, 282).

The methyl ether of allylcarbinol, $CH_2:CH\cdot CH_2\cdot CH_2\cdot OMe$, D^0 0·817, D^{20} 0·8, n_D^{20} 1·398, b. p. 68—69°, was prepared by the action of zinc dust in alcohol on $\gamma\delta$-dibromobutyl methyl ether, n_D^{20} 1·5158, b. p. 96°/16 mm. (compare Lespieau, Abstr., 1907, i, 580). $\gamma\delta$-Dibromobutyl ethyl ether, D^0 1·662, D^{20} 1·614, n_D^{20} 1·498, b. p. 98°/12 mm. (compare Abstr., 1910, i, 353), on treatment with hydrogen bromide forms only $\beta\delta$-dibromobutane, D^{20} 1·80, n_D^{20} 1·507, b. p. 64°/13 mm. (compare Demjanoff, Abstr., 1895, i, 161). The *phenylurethane* of allyl alcohol has m. p. 70° and is crystalline; that of allylcarbinol is a syrup.

$\alpha\beta\delta$-Tribromobutane, D^0 2·276, D^{18} 2·234, n_D^{18} 1·574, prepared as described already (Abstr., 1908, i, 496), when heated with boiling water or moist silver oxide gives 3-hydroxytetrahydrofuran (Abstr., 1909, i, 691), D^0 1·107, D^{18} 1·07, n_D^{18} 1·4478, MR 21·91 (calc., 21·61), a colourless, syrupy liquid, and with potassium acetate solution yields the triacetin of $\alpha\beta\delta$-trihydroxybutane, D^0 1·152, D^{19} 1·13, n_D^{19} 1·436, b. p. 150°/11 mm., or 158°/17 mm., which on hydrolysis by baryta gives the trihydric alcohol, D^0 1·21, D^{20} 1·18, n_D^{20} 1·47, b. p. 179°/13 mm. (compare Wagner, *loc. cit.*). This yields a *triphenylurethane*, m. p. 149—152°, in colourless needles, and a *δ-ethyl ether*, D^0 1·08, n_D^{15} 1·45, b. p. 130°/14 mm., of which the *diphenylurethane* is crystalline, and melts at 98—99°. In the formation of this ether, as in that of the methyl ether, some 3-hydroxytetrahydrofuran is formed (Abstr., 1909, i, 691). $\gamma\delta$-Dibromobutyl alcohol, D^0 2·02, D^{15} 1·98, n_D^{15} 1·548, b. p. 114°/11 mm. (compare Wagner, *loc. cit.*, and Abstr., 1909, i, 282), gives a *phenylurethane*, m. p. 70—71°. α-Bromo-Δ^{γ}-butylene oxide with (1) potassium acetate gives the diacetin of $\alpha\beta\delta$-trihydroxybutane (Abstr., 1909, i, 691), D^0 1·17, D^{16} 1·15, n_D^{16} 1·446, b. p. 161—163°/18 mm.; (2) acetic anhydride and zinc chloride yields *α-bromo-γδ-diacetoxybutane*, $CH_2Ac\cdot CHAc\cdot CH_2\cdot CH_2Br$, D^{20} 1·44, n_D^{20} 1·473, b. p. 140—141°/13—14 mm., a colourless liquid, having an odour like that of ethyl acetate, and (3) with potassium acetate furnishes α-acetoxy-Δ^{γ}-butylene oxide, $\overset{CH_2}{\underset{O}{|}}\!\!>CH\cdot CH_2\cdot CH_2\cdot OAc$, D^{18} 1·12, n_D^{18} 1·446, b. p. 189—192°, a colourless liquid having an odour recalling that of ethyl acetate. α-Ethoxy-Δ^{γ}-butylene oxide, D^0 0·957, D^{18} 0·934, n_D^{18} 1·415 (Abstr., 1910, i, 353), is converted by hydrogen chloride into α-chloro-β-hydroxy-δ-ethoxybutane.

Δ^{α}-Butylene-γδ-oxide, $\overset{CH_2}{\underset{O}{|}}\!\!>CH\cdot CH:CH_2$, precipitates a solution of magnesium chloride in alcohol and water, polymerises readily, is easily hydrated to form erythrol, from which natural and racemic erythritols may be prepared (compare Abstr., 1910, i, 463), and on

treatment with bromine in chloroform gives *αβ-dibromo-Δ^{γ}-butylene oxide*, D^0 2·028, n_D^{22} 1·542, b. p. 99°/13—14 mm. The latter with hydrogen bromide in chloroform gives *αγδ-tribromo-β-hydroxybutane*, b. p. 148—150°/14 mm. This in turn reacts with phosphorus pentabromide at 150° to give αβγδ-tetrabromobutane, m. p. 117—119°, crystallising in colourless needles (compare Griner, Abstr., 1893, 237). Ciamician and Magnaghi's form of this substance, m. p. 38—39° (Abstr., 1886, 521), was not obtained. By the action of bromine on erythrol [Δ^{α}-butylene-γδ-diol], two αβ-dibromo-γδ-dihydroxybutanes, the one crystalline, m. p. 88—89·5°, and probably identical with that of Grimaux and Cloez (Abstr., 1890, 730) and the other liquid, are formed. T. A. H.

Chloro-ethers. VI. αβ-Dichloro-*n*-propyl Ether, αββ′-Trichloro-*n*-propyl Ether, and Tetrachloro-*n*-propyl Ether. GIUSEPPE ODDO and GUIDO CUSMANO (*Gazzetta*, 1911, 41, ii, 224—245. Compare Oddo and Mameli, Abstr., 1904, i, 280; 1906, i, 134, 619; and the two following abstracts).—In the present paper the authors continue the study of the above dichloro- and trichloro-ethers, recording new decomposition products and condensations, and describe also a tetrachloro-ether.

In the chlorination of *n*-propyl ether in diffuse light at 25°, in addition to the dichloro-ether, the following substances are produced in small quantities: (1) α-monochloropropaldehyde; (2) a substance, b. p. 144—147°, probably a *monochloropropyl ether*; (3) the trichloro-ether. When the dichloropropyl ether is treated with sulphuric acid at 135—140°, α-chloropropaldehyde, b. p. 85—86°, is obtained (compare Brochet, Abstr., 1896, i, 114). This aldehyde polymerises readily on keeping (although it is stable in a sealed tube); the *polymeride* is a white powder, which does not melt, but is reconverted into the liquid aldehyde at 170—200°. It appears to form a compound with water, but the hydrate could not be obtained in a crystalline state. It also forms an alcoholate with propyl alcohol, but this also was not isolated.

When αβ-dichloro-*n*-propyl ether is boiled with water and the product fractionated, α-chloropropaldehyde and β-chloropropacetal, $CHMeCl\cdot CH(OPr)_2$, are obtained. The action of propyl alcohol also results in the formation of the latter substance.

When αβ-dichloro-*n*-propyl ether is boiled for about one hundred hours, n-*propyl-β-chloropropylene ether*, $CMeCl\colon CH\cdot OPr$, is obtained as a colourless liquid, b. p. 145—146·5°. The action of bromine on this unsaturated compound yields *β-chloro-αβ-dibromopropyl ether*,

$$CMeClBr\cdot CHBr\cdot OPr,$$

which is a mobile liquid, b. p. 140—142°/20 mm. With pyridine it yields a *compound*, m. p. 216—217°, which gives a *platinichloride*, m. p. also 216—217°.

In view of the above reactions it is shown that the dichloro-ether is αβ-dichloro-*n*-propyl ether, and this is confirmed by its synthesis from α-chloropropaldehyde, propyl alcohol, and hydrogen chloride.

αββ′-Trichloro-*n*-propyl ether is obtained mixed with the tetrachloro-ether by chlorinating *n*-propyl ether or αβ-dichloro-*n*-propyl

ether on a boiling brine-bath; it has b. p. 115—120°/5—10 mm. When heated with sulphuric acid it yields α-chloropropaldehyde; with carbamide or urethane it gives the same products as the dichloro-ether. One chlorine atom is removed by silver nitrate, showing that it occupies the α-position, and this is confirmed by its behaviour with pyridine, which yields a compound of which the *platinichloride* (orange-yellow crystals, m. p. 187°) has the composition

$$(C_6H_{11}OCl_3 \cdot C_5H_5N)_2PtCl_4.$$

The constitution of the trichloro-ether follows from these reactions, from its modes of formation, and from its synthesis from β-chloropropaldehyde, allyl alcohol, and hydrogen chloride.

The *tetrachloro*-n-*propyl ether* obtained in the preparation of the trichloro-ether is a colourless, oily liquid, b. p. 157—162°/5—10 mm. With sulphuric acid and with silver nitrate, it behaves like the mono- and di-chloro-ethers. It gives a pyridine compound, of which the *platinichloride*, $(C_6H_{10}OCl_4,C_5H_5N)_2,PtCl_4$, forms orange-yellow crystals, m. p. 187°. R. V. S.

Chloro-ethers. VII. Aldehydic Condensations by means of Halogenated Ethers. GIUSEPPE ODDO and GUIDO CUSMANO (*Gazzetta*, 1911, 41, ii, 246—258. Compare preceding abstract).—Carbamide reacts with dichloroacetaldehyde or its polymeride in aqueous solution, yielding *α-hydroxy-ββ-dichloroethylcarbamide*, which forms crusts of prismatic crystals, m. p. 142° (decomp.). αββ-Trichloroethyl ether and carbamide in presence of sodium acetate yield the same condensation product.

Hydrazine hydrate reacts with dichloroacetaldehyde, with its polymeride, and with αββ-trichloroethyl ether, giving an amorphous, reddish-yellow powder, which does not melt at 300°.

Semicarbazide reacts with the same three ethers, yielding a substance, $C_4H_5O_2N_5$, which is an amorphous, yellowish-white powder.

Phenylhydrazine with dichloroacetaldehyde or αββ-trichloroethyl ether forms glyoxalosazone.

Carbamide and α-chloropropaldehyde yield a white, amorphous substance, m. p. 167—170° (decomp.), which is also formed when carbamide reacts with αβ-dichloro-, αββ′-trichloro-, or tetrachloro-*n*-propyl ether.

Urethane reacts with α-chloropropaldehyde, αβ-dichloro-, αββ′-trichloro- and tetrachloro-*n*-propyl ether, giving in all cases *β-chloropropylidenebisurethane*, $CHMeCl \cdot CH(NH \cdot CO_2Et)_2$, which forms tufts of long, colourless needles, m. p. 122—123°.

Urethane and β-chloro-αβ-dibromo-*n*-propyl ether yield *β-chlorobromopropylidenebisurethane*, $CMeClBr \cdot CH(NH \cdot CO_2Et)_2$, which crystallises in small, transparent prisms, m. p. 113—115°. The above chlorobromo-ether, when treated with carbamide, gives an aldehydic compound crystallising in minute needles, m. p. 183—184°.

R. V. S.

Catalytic Actions of Sulphuric Acid. I. GIUSEPPE ODDO (*Gazzetta*, 1911, 41, ii, 258—267. Compare preceding abstracts).—When the halogenated ethers and some related substances are dropped

on concentrated sulphuric acid at a high temperature, the corresponding aldehydes are formed.

[With Efisio Mameli.]—Dichloroacetaldehyde is obtained from any of the following substances when dropped on concentrated sulphuric acid at 140—145°: *αββ*-trichloroethyl ether, dichloroacetaldehyde hydrate, dichloroacetal, and ethyl dichlorovinyl ether (compare Abstr., 1904, i, 280; Wohl and Roth, Abstr., 1907, i, 170).

[With Guido Cusmano.]—*α*-Chloropropaldehyde is obtained by the action of concentrated sulphuric acid at 135—140° on the following substances: *αβ*-dichloro-, *αββ'*-trichloro- and tetrachloro-*n*-propyl ether, di-*n*-propyl-*β*-chloropropylidene ether, and *n*-propyl-*β*-chloropropylene ether.

[With Eugenia Mantovani.]—When ethyl acetoacetate is dropped on sulphuric acid at 155—165°, keten appears to be formed, but is resinified by the acid; at the same time much ethyl acetate is produced. The decomposition of ethyl malonate with sulphuric acid at 200° yields carbon dioxide, ethylene, and ethyl acetate. Ethyl succinate is not acted on below 240—250°, and is then merely hydrolysed, ethyl alcohol and succinic acid being obtained.

R. V. S.

Nitrogen and Sulphur Derivatives of Carbon Disulphide. XVIII. Chlorothiocarbonates. Marcel Delépine (*Bull. Soc. chim.*, 1911, [iv], 9, 901—903. Compare Klason, Abstr., 1887, 1029). —The methyl, ethyl, and propyl esters have been prepared by Klason's method (*loc. cit.*) and are described.

The alcohol (2 mols.) is added gradually to thiocarbonyl chloride at atmospheric temperature, and after twelve to twenty-four hours ether is added, and finally water. The oily layer is separated, washed with water, dried over calcium chloride, and rectified by distillation in carbon dioxide. The yield of the methyl and ethyl esters is about 50% of the theoretical, but is very small in the case of the propyl ester. The esters are pale yellow liquids of pungent ozone-like odour; they fume in the air, owing to oxidation and the liberation of sulphuric acid; they are luminous in the dark, the propyl ester being least luminous. With amines they react according to the equation: $2R_1R_2NH + Cl{\cdot}CS{\cdot}OR' = R_1R_2N{\cdot}CSOR' + R_1H_2NH,HCl$, where R_1 or R_2 may be a hydrogen atom. With secondary amines they give dialkylthiocarbamates (Abstr., 1910, i, 720).

Methyl chlorothiocarbonate, $CSCl{\cdot}OMe$, has D_4^0 1·2975, D_4^{22} 1·2686, and b. p. 107—108°. Ethyl chlorothiocarbonate has D_4^0 1·2138, D_4^{15} 1·1955, b. p. 127—128° (compare Klason, *loc. cit.*). *Propyl chlorothiocarbonate*, $CS{\cdot}Cl{\cdot}OPr^a$, b. p. 148—151°, reacts with aniline to form propyl phenylthiocarbamate (Orndorff and Richmond, Abstr., 1900, i, 156), which is best obtained by Roschdestvensky's method (Abstr., 1909, i, 300).

T. A. H.

Some Compounds of Organic Salts of Bivalent Metals with Ammonia, Pyridine, and Phenylhydrazine. Hermann Grossmann and Gustav Jäger (*Zeitsch. anorg. Chem.*, 1911, 73, 48—74).—For the purpose of investigating the influence of the acid radicle on the type of additive compound formed by salts (compare Grossmann

and Hünseler, Abstr., 1906, i, 7), the additive compounds of a number of salts of organic acids have been prepared. The ammonia compounds are usually prepared by dissolving the hydrated salt in 25% aqueous ammonia, filtering, and evaporating, first on a water-bath and then in a desiccator over sodium hydroxide in an atmosphere of ammonia.

Ammonia cupric formate, $Cu(HCO_2)_2,3NH_3$, forms large, blue prisms or slender needles, m. p. 154°. The compound is stable in air, but is decomposed by water. *Ammonia cupric chloroacetate*,

$$Cu(CH_2Cl \cdot CO_2)_2,2NH_3,H_2O,$$

forms a blue, crystalline powder, m. p. 180° (decomp.). *Ammonia cupric trichloroacetate*, $Cu(CCl_3 \cdot CO_2)_2,5NH_3$, forms dark bluish-violet crystals, which lose ammonia suddenly, becoming grass-green at 94° and melting at 98°. After six weeks in air the crystals contain $3NH_3$. *Ammonia zinc formate*, $Zn(HCO_2)_2,2\frac{1}{2}NH_3$, forms colourless, prismatic needles, m. p. 126°. *Ammonia zinc acetate*,

$$Zn(C_2H_3O_2)_2,6NH_3,5H_2O,$$

forms colourless needles. *Ammonia cadmium formate*,

$$Cd(HCO_2)_2,3NH_3,3H_2O,$$

forms transparent crystals, m. p. 70°, and loses NH_3 and H_2O in air. *Ammonia cadmium acetate*, $Cd(C_2H_3O_2)_2,4NH_3$, forms transparent cubes, m. p. 141°, and loses NH_3 in air. *Ammonia nickel formate*, $Ni(HCO_2)_2,3NH_3,2H_2O$, is a bright blue, crystalline powder, becoming green at 120° and charring at 360°, three other additive compounds of the salt being also obtained, containing $4NH_3,2H_2O$, $3NH_3,H_2O$, and $2NH_3$ respectively. *Ammonia nickel acetate*, $Ni(C_2H_3O_2)_2,2NH_3$, is a green precipitate; a definite compound could not be obtained from the chloroacetate. *Ammonia nickel trichloroacetate*,

$$Ni(CCl_3 \cdot CO_2)_2,3NH_3,3H_2O,$$

forms blue crystals, and becomes green in air, losing $2NH_3$ and $3H_2O$.

Pyridine cupric formate, $Cu(HCO_2)_2,3C_5NH_5$, forms blue needles, m. p. 103°, and loses pyridine in air. Two *pyridine cupric acetates* are obtained, $Cu(C_2H_3O_2)_2,5C_5NH_5$ being bright green, and

$$Cu(C_2H_3O_2)_2.6C_5NH_5$$

dark violet. *Pyridine cupric chloroacetate*,

$$Cu(CH_2Cl \cdot CO_2)_2,2C_5NH_5,2H_2O,$$

forms blue crystals, and a second compound is also obtained. *Pyridine cupric trichloroacetate*, $Cu(CCl_3 \cdot CO_2)_2,4C_5NH_5,2H_2O$, forms sky-blue needles. *Pyridine zinc formate*, $Zn(HCO_2)_2,2C_5NH_5$, loses pyridine in air, whilst zinc acetate yields only unstable products. *Pyridine cadmium formate*, $Cd(HCO_2)_2,3C_5NH_5$, has m. p. 94°, and loses pyridine in air. *Pyridine nickel formate*, $Ni(HCO_2)_2,3C_5NH_5$, is a pale green, crystalline powder, which blackens without melting; *pyridine cobalt formate*, $Co(HCO_2)_2,3C_5NH_5$, is pale pink, and is stable in air, but loses pyridine after some months.

Phenylhydrazine zinc formate, $Zn(HCO_2)_2,2C_6H_8N_2$, is a white solid, m. p. 110°, which rapidly darkens in air. *Phenylhydrazine cadmium formate*, $Cd(HCO_2)_2,C_6H_8N_2$, has m. p. 128°; *phenylhydrazine nickel formate*, $Ni(HCO_2)_2,C_6H_8N_2,3H_2O$, a bluish-green, amorphous mass, blackens without melting, a blue product being also obtained, probably containing $2C_6H_8N_2$. *Phenylhydrazine cobalt formate*, $Co(HCO_2)_2,2C_6H_8N_2$,

is a pink substance, m. p. 170—172°, which darkens in air. *Phenylhydrazine cobalt acetate*, $Co(C_2H_3O_2)_2,4C_6H_8N_2$ (compare Moitessier, Abstr., 1897, i, 561), is unstable; *phenylhydrazine cobalt chloroacetate*, $Co(CH_2ClCO_2)_2,3C_6H_8N_2$, and *phenylhydrazine cobalt trichloroacetate*, $Co(CCl_3CO_2)_2,6C_6H_8N_2$, m. p. 188°, are pink solids. A tabular summary of the compounds of this series is given. C. H. D.

The Hydrates of Potassium Acetate, their Solubility and Transition Point. RYUJI ABE (*Mem. Coll. Sci. Eng. Kyōtō*, 1911, 3, 211—215).—The solubility curve of potassium acetate in water has a single break at 41·3°, the stable phase at lower temperatures being $2KC_2H_3O_2,3H_2O$, and at higher temperatures, $2KC_2H_3O_2,H_2O$.

C. H. D.

Aliphatic Nitro-compounds. XI. α-Nitro*iso*butyric Acid. WILHELM STEINKOPF and ALEXANDER SUPAN (*Ber.*, 1911, 44, 2891—2897).—α-Nitro*iso*butyric acid has been prepared by the following series of operations: α-Hydroxylamino*iso*butyronitrile, obtained by the addition of hydrogen cyanide to acetoxime, was oxidised with potassium permanganate in sulphuric acid to α-nitro*iso*butyronitrile (Piloty, Abstr., 1898, i, 616). This cannot be hydrolysed directly, but on heating with methyl alcohol and hydrochloric acid, it is converted almost quantitatively into the hydrochloride of nitro*iso*butyroiminomethyl ether,

$$NO_2\cdot CMe_2\cdot C(NH)\cdot OMe,HCl.$$

This is decomposed by water into methyl-α-nitro*iso*butyrate, $NO_2\cdot CMe_2\cdot CO_2Me$, a colourless oil, which with ammonia forms α-nitro*iso*butyramide, and when left for some days with concentrated hydrochloric acid is slowly hydrolysed to α-nitro*iso*butyric acid.

When the ammonium salt is treated with sodium nitrite and sulphuric acid, carbon dioxide is eliminated and a blue oil formed, which solidifies to colourless crystals of propyl ψ-nitrol,

$$NO\cdot CMe_2\cdot NO_2.$$

α-Nitro*iso*butyric acid differs from nitroacetic and α-nitropropionic acids in not being hygroscopic. On prolonged keeping, it decomposes to a blue oil mixed with colourless crystals, which melt to a blue liquid, and nitrous acid is liberated. This is a nitroso-compound, but it has not at present been identified. When fused, α-nitro*iso*butyric acid liberates carbon dioxide and forms a colourless oil, which suddenly decomposes, becoming blue and solidifying to a colourless solid. Similar changes are noted on heating in solvents. Possibly the acid decomposes into *sec.-aci*-nitropropane, this into acetone and nitrosyl, which re-unite to a nitroso-alcohol, $NO\cdot CMe_2\cdot OH$.

α-Nitro*iso*butyronitrile is an oil, b. p. 73°/12 mm. *Methyl-α-nitro*iso*butyric acid* has b. p. 73—74°/12 mm. *α-Nitro*iso*butyric acid* forms crystals, m. p. 95°; the *ammonium*, *sodium*, and *phenylhydrazine* salts have been prepared. E. F. A.

Action of Hydrogen Chloride and Methyl Alcohol on Negatively Substituted Nitriles. WILHELM STEINKOPF and WIATSCHESLAW MALINOWSKI (*Ber.*, 1911, 44, 2898—2904).—Whilst

Pinner has shown that, in general, both aromatic and aliphatic imino-ether hydrochlorides are obtained by the reaction of nitrile, alcohol, and hydrogen chloride, Steinkopf obtained trichloroacetamide from trichloroacetonitrile (Abstr., 1907, i, 488) and nitroacetamide from nitroacetonitrile (Abstr., 1909, i, 216), instead of the expected imino-ethers. On the other hand, Steinkopf and Supan (preceding abstract) find that *a*-nitro*iso*butyronitrile gives the normal imino-methyl ether and not the amide. The influence of the negative nitro-group appears to be less when the nitro-group is tertiary.

The behaviour of a number of halogen substituted acetonitriles towards methyl alcohol and hydrogen chloride has now been investigated. Chloro-, bromo- and iodo-acetonitrile give the normal imino-ether hydrochloride; dibromoacetonitrile yields a mixture of imino-ether and dibromoacetamide.

Dichloro-, trichloro-, dichloronitro-, and tribromo-acetonitrile all yield the corresponding amides, no trace of imino-ether being formed.

The primary nitro-group is as active as two or three chlorine atoms; this is probably owing to its reacting in the *aci*-form.

With trichloroacetonitrile and dimethylethylcarbinol only the corresponding amide was obtained. The imino-ether could not be obtained on boiling tribromoacetonitrile with methyl alcohol.

[With ALEXANDER SUPAN.]—*ω-Nitrophenylacetonitrile* was obtained pure in colourless crystals, m. p. 39—40°, from the sodium salt Wislicenus, Abstr., 1902, i, 541). E. F. A.

Oxidation of Hexoic and Heptoic Acids by Dilute Permanganate Solutions. E. S. PRSCHEVALSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1000—1006).—Oxidation of *n*-hexoic acid with 1% neutral permanganate solution in the cold yields butyric, valeric, oxalic, and succinic acids.

Under similar conditions, *n*-heptoic acid gives oxalic, succinic, propionic, butyric, and valeric acids; further, the action of semicarbazide hydrochloride on that portion of the oxidation products which dissolves readily in ether, water, alcohol, chloroform, and acetone yields two isomeric semicarbazones, $C_8H_{15}O_3N_3$, one, m. p. 138—140°, readily soluble, and the other, m. p 176°, slightly soluble. These represent semicarbazones of a keto-acid, $C_7H_{12}O_3$, which must be regarded as an intermediate product in the oxidation of *n*-heptoic acid. T. H. P.

Preparation of Diglycollic Acid Esters of Phenols and Phenolic Derivatives. C. F. BOEHRINGER & SÖHNE (D.R.-P. 236045).—Phenolic esters of diglycollic acid prepared from the acid dichloride have been described (Abstr., 1910, i, 732); it is now found that this reaction proceeds smoothly with the acid on gently warming in the presence of phosphorus pentachloride and an indifferent base, the phenyl ester being thus obtained in 90% yield. The *o-tolyl* ester has m. p. 100—101°. F. M. G. M.

Studies on Tautomerism. VI. Colorimetric Method for the Estimation of Enols in Allelotropic Mixtures. LUDWIG KNORR and H. SCHUBERT (*Ber.*, 1911, **44**, 2772—2778. Compare Wislicenus, Abstr., 1900, i, 9, 597).—By colorimetric comparison of the solutions obtained on adding ferric chloride to equilibrium mixtures of tautomeric substances, the amount of enolic form present can be estimated. The maximum coloration is produced when 1 mol. of ferric chloride reacts with the enol, the corresponding equation being $RH + FeCl_3 = FeRCl_2 + HCl$, where R is the enolic residue. Standard solutions of three kinds are employed: (1) when the pure enolic form is available, a solution of it containing an equimolecular quantity of sublimed ferric chloride; (2) solutions of the iron salts of the type FeR_3 (see below), to which 2 mols. of ferric chloride have been added ($FeR_3 + 2FeCl_3 = 3FeCl_2R$), and in addition, to make them identical with those of the first type, 3 mols. of hydrochloric acid; (3) solutions (usually alcoholic) of equilibrium mixtures to which 1 mol. of ferric chloride has been added, the amount of the enolic form present having been determined by comparison with test solutions of one of the first two types. The standard solutions of the third kind often remain unaltered for months. The solutions of types I. and II. also suffer no marked alteration on keeping, unless (as in the case of dibenzoylacetylmethane, for instance) decomposition occurs; hence the enolic forms may be fixed in the form of their iron salts. In some cases (ethyl acetoacetate and especially ethyl benzoylacetate) the addition of hydrochloric acid to the iron salts lessens the intensity of colour of the solution; in other cases (tribenzoylmethane) no change is observed. The standard solutions of the second type have exactly the same degree of coloration as those of type I.

The method has been employed for the study of the diacetylsuccinic ester, mesityl-oxide-oxalic esters, and Claisen's triketones. In the present paper experimental data are given in the case of methyl mesityl-oxide-oxalate. In the fused state at 98° the enolic ester reaches equilibrium (4% enol) after twenty-five hours, whilst the ketonic ester attains to the same equilibrium in two hundred hours. In absolute alcoholic solution at 78° equilibrium is reached (3·7% enol) after twelve days, whilst the ketonic form contains 3·9% enol after twenty days. In absolute alcohol at room temperature, the enolic ester is converted into the equilibrium mixture (4% enol) after eight weeks. Determinations were also made of the equilibria reached in different solvents after fourteen days at 80°.

Some new iron salts have been prepared (compare Hantzsch and Desch, Abstr., 1902, i, 708; also this vol., i, 976). *Ethyl ferriacetoacetate*, $Fe(C_6H_9O_3)_3$ (from an alcoholic solution of ethyl sodioacetoacetate and an ethereal solution of ferric chloride), forms small, compact, red crystals, m. p. 99—100°. The solutions of the salt are orange-coloured, and become cherry-red on addition of ferric chloride.

Ethyl ferriformylphenylacetate, $Fe(C_{11}H_{11}O_3)_3$, is obtained in a crystalline condition by treating an ethereal solution of the ester with

an alcoholic solution of sodium ethoxide and ferric chloride in the presence of sodium acetate. R. V. S.

Lactarinic Acid. J. BOUGAULT and CHARLES CHARAUX (*Compt. rend.*, 1911, **153**, 880—881. Compare this vol., i, 835).—Lactarinic acid is identical with *ε-ketostearic acid*,

$$CH_3\cdot[CH_2]_{11}\cdot CO\cdot[CH_2]_4\cdot CO_2H,$$

since it undergoes the Beckmann transformation, giving rise to two compounds, $CH_3\cdot[CH_2]_{11}\cdot NH\cdot CO\cdot[CH_2]_4\cdot CO_2H$ and

$$CH_3\cdot[CH_2]_{11}\cdot CO\cdot NH\cdot[CH_2]_4\cdot CO_2H.$$

These were not isolated, but recognised by the products obtained on hydrolysis. W. O. W.

Synthesis of Fumaric and Maleic Acids from the Acetylene Di-iodides. EDWARD H. KEISER and LEROY MCMASTER (*Amer. Chem. J.*, 1911, **46**, 518—523).—Keiser (Abstr., 1890, 594) has shown that fumaric acid can be produced by the action of potassium cyanide and potassium hydroxide on solid acetylene di-iodide. The same author (Abstr., 1899, i, 398) has also obtained a liquid form of acetylene di-iodide, which he regarded as the *cis*- or maleic form, whilst the solid compound was regarded as the *trans*- or fumaric isomeride.

This view has now been confirmed, and experiments are described which show conclusively that the solid iodide can be converted into fumaric acid and the liquid isomeride into maleic acid. E. G.

Nitrile of Fumaric Acid. EDWARD H. KEISER and J. J. KESSLER (*Amer. Chem. J.*, 1911, **46**, 523—528).—Keiser (Abstr., 1890, 594) and Keiser and McMaster (preceding abstract) have shown that fumaric and maleic acids can be prepared by treating the solid and liquid forms of acetylene di-iodide respectively with potassium cyanide and hydroxide. It is evident that in these syntheses the nitriles of the acids must be formed, but they could not be isolated.

Attempts have therefore been made to prepare the nitriles by heating fumaramide and ammonium maleate with phosphoric oxide. Fumaronitrile has been produced in this way, but maleonitrile could not be obtained.

Fumaramide is prepared (1) by treating ethyl bromosuccinate with dilute ammonia, and (2) by the action of 50% ammonia solution on dimethyl fumarate. When an intimate mixture of fumaramide and phosphoric oxide is heated on a sand-bath at about 120°, *fumaronitrile*, m. p. 96°, b. p. 186°/760 mm., is obtained as a sublimate of slender needles. The nitrile has a pleasant, pungent odour, sublimes readily even below 100°, and is decomposed by alkali hydroxide with formation of alkali cyanide. E. G.

Hydrogenation of Crotonaldehyde in Presence of Nickel. ROGER DOURIS (*Bull. Soc. chim.*, 1911, [iv], **9**, 922—925).—On reduction by Sabatier and Senderens' method (Abstr., 1905, i, 333), crotonaldehyde furnishes butyraldehyde and butyl alcohol with a small quantity of a syrupy substance, b. p. 115—119°/18 mm., which may contain an octyl alcohol.

n-*Butylidenediurethane*, $CHPr^{a}(NH\cdot CO_2Et)_2$, m. p. 130°, obtained by condensing butyraldehyde with urethane in presence of hydrochloric acid, crystallises in rosettes of colourless needles. n-*Butyl phenylthiocarbamate*, $NHPh\cdot CS\cdot O\cdot C_4H_9$, m. p. 53°, obtained by Roschdestvensky's method (Abstr., 1910, i, 107) or by the action of phenylthiocarbimide on *n*-butyl alcohol in presence of sodium hydroxide, crystallises in long, colourless needles. T. A. H.

Ethylation of Acetone. ERNST ZERNER (*Monatsh.*, 1911, 32, 677—686).—By the action of sodamide and halogen alkyls on ketones, alkyl derivatives of these are obtained. Haller and Bauer (Abstr., 1909, i, 108) have thus prepared methyl and mixed methyl ethyl derivatives of acetone. Acetone itself yields only condensation products, particularly *iso*phorone, when treated with sodamide and ethyl bromide. Accordingly, dipropyl ketone was used as the starting-point for the preparation of ethyl derivatives of acetone. In ethereal solution no action takes place, but in benzene prolonged boiling suffices to cause interaction. About half of the dipropyl ketone is recovered unchanged, and the operation has to be repeated several times. Other products are not formed in any quantity, and the ketones are separated and purified by fractional distillation. The process is repeated in order to pass to the more alkylated ketones.

The ethylacetones described do not mix with water and have a camphor-like odour; only hexaethylacetone resembles the fruity odour of dipropyl ketone. The corresponding alcohols have a sharp, peppermint-like odour.

Triethylacetone [γ-ethylheptane-δ-one], perhaps already obtained by Geuther and Frölich (Abstr., 1880, 622), has b. p. 174·5—175·5°/741 mm. On reduction it yields *triethyl*iso*propyl alcohol* [*γ-ethylheptane-δ-ol*], which has b. p. 80—81°/10 mm. The *oxime* obtained by heating the ketone with Crismer's salt formed slender needles, m. p. 90—91°.

sym-Tetraethylacetone [γε-diethylheptane-δ-one] has b. p. 206—207·5°/771 mm. (Herzig and Zeisel, Abstr., 1894, i, 74). It does not form an oxime or phenylhydrazone. *Tetraethyl*iso*propyl alcohol* [*γε-diethylheptane-δ-ol*], obtained on reduction, has b. p. 99—101°/13 mm.; it reacts with phenylcarbimide, forming the *phenylurethane*, m. p. 72—73°.

Pentaethylacetone [*γγε-triethylheptane-δ-one*] has b. p. 237·5—238·5°/761 mm.; *pentaethyl*iso*propyl alcohol* [*γγε-triethylheptane-δ-ol*] has b. p. 125—127°/18 mm., and forms a *phenylurethane*, m. p. 71—72°. The mixture of the phenylurethane with that of the γε-diethylheptane-δ-ol shows a depression of 18° in the m. p.

Hexaethylacetone [*γγεε-tetraethylheptane-δ-one*] has b. p. 274—275°/759 mm., and crystallises in plates, m. p. 44°. The corresponding *hexaethyl*iso*propyl alcohol* [*γγεε-tetraethylheptane-δ-ol*] has b. p. 159—161°/18 mm. The *phenylurethane* forms a butter-like substance, which is not characteristic. E. F. A.

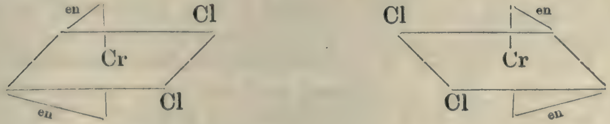
An Intermediate Product of Alcoholic Fermentation. HANS VON EULER and A. FODOR (*Biochem. Zeitsch.*, 1911, 36, 401—410).—The authors fail to confirm Boyson-Jenssen's statement that dihydroxy-

acetone can be isolated as an intermediate product of fermentation by yeast. They describe their method for preparing hexosephosphoric acid ester, and their results obtained with this substance agree in the main with those of Harden and Young. They have found indications that in addition to the hexosediphosphoric acid, a triosemonophosphoric acid is also formed (compare Young, Abstr., 1910, i, 12; Lebedeff, *ibid.*, 716; this vol., i, 837). S. B. S.

Decomposition of Dextrose by Dilute Sulphuric Acid. Hermann Ost and Th. Brodtkorb (*Chem. Zeit.*, 1911, 35, 1125—1126. Compare Ost and Wilkening, Abstr., 1910, i, 364).—Dextrose is converted by dilute sulphuric acid under pressure at high temperatures chiefly into humin substances, formic acid, and lævulic acid; for example, about 8% of the dextrose is destroyed by heating a 5% solution of the sugar with a 2% solution of sulphuric acid for twenty-four hours at 100°, whilst 100 grams of dextrose heated with 2% sulphuric acid at 140° for seven hours yield about 16 grams of formic acid, 32 grams of lævulic acid, and 13 grams of humin substances. W. H. G.

The Behaviour of Invert Sugar in Alkaline Solution in Presence of Hydrogen Peroxide. Adolf Jolles (*Biochem. Zeitsch.*, 1911, 36, 389—393).—In following the polarisation changes when invert sugar is treated with hydrogen peroxide in alkaline solutions, it is found that the rotation sinks gradually to 0°, then becomes dextrorotatory, the dextrorotation then reaches a maximum, and again decreases. The explanation of this result is that lævulose is more readily oxidised than dextrose, and is more rapidly destroyed. S. B. S.

Mirror Image Isomerism with Chromium Compounds. I. Alfred Werner (*Ber.*, 1911, 44, 3132—3140).—The author has succeeded in resolving salts of the 1 : 2-dichlorodiethylenediamine-chromium series into their optical isomerides, in accordance with the configurations:



These salts present a case of molecular asymmetry I, similar to that observed with the 1 : 2-dinitrodiethylenediaminecobalt salts (this vol., i, 838). Owing to the fact that the aqueous solutions of these salts are not very stable, readily giving chloro-aquo- and diaquo-salts, their resolution with silver bromocamphorsulphonate did not afford much hope of success. It was found, however, that when *d*-ammonium α-bromocamphorsulphonate was added to a freshly-prepared saturated solution of 1 : 2-dichlorodiethylenediaminechromic chloride, violet crystals of l-*dichlorodiethylenediaminechromic* d-α-*bromocamphorsulphonate* were deposited after a short time in a pure condition. From the

mother liquor, any racemate could then be precipitated as dithionate, and then, on the addition of potassium platinochloride, the *d*-isomeride obtained as the platinochloride, from which the nitrate could be prepared by decomposition with silver nitrate. Similar results were obtained with *l*-ammonium α-bromocamphorsulphonate, d-*dichlorodiethylenediaminechromic* l-α-*bromocamphorsulphonate* being first deposited.

It is noteworthy that the *l*-dichloro-salts and *d*-bromocamphorsulphonic acid, and the *d*-dichloro-salts and *l*-bromocamphorsulphonic acid, give the least soluble salts, which is the opposite to what was observed with the cobalt salts.

The active salts are not different in colour from the inactive, but the active chlorides and dithionates are more soluble than the corresponding racemates.

The optical rotation observed are as follows (I.):

	I.		II.	
	[α].	[M].	[α].	[M].
Chloride	−140°	−415·1°	−182°	−552·4°
	+140	+415·1	+184	+558
Bromide	−130	−419·9	−176	−571
	+124	+400·5	+168	+554
Iodide	−120	−366	−164	−511
	+122	+372	+164	+511

They are much less than those of the corresponding dichlorodiethylenediaminecobalt salts (II.) (details are to be given later).

Racemisation takes place rapidly in aqueous solution, being complete at 0° after three hours in a 0·5% solution; in hydrochloric acid solution the velocity of racemisation is much slower, and at the same time the rotation of the chloride is much diminished.

Racemic 1:2-dichlorodiethylenediaminechromic chloride, $[Cl_2Cr\,en_2]Cl$, is best prepared as follows: Potassium chromium oxalate,

$$[Cr(C_2O_4)_3]K_3,$$

is heated with a 10% solution of ethylenediamine until a red salt begins to deposit from the dark violet solution. After cooling, the salt, which has the formula $[C_2O_4Cr\,en_2][(C_2O_4)_2Cr\,en]$, is collected, well washed with cold water, rubbed into a paste with concentrated hydrochloric acid, and kept until a portion when dried on a porous plate leaves a yellow residue of oxalatodiethylenediaminechromic chloride, $[C_2O_4Cr\,en_2]Cl$. This is collected and carefully heated with concentrated hydrochloric acid until solution is complete. The cherry-red solution so obtained is put into a crystallising dish, and alcohol added gradually, with vigorous stirring, nntil a violet salt begins to deposit. On keeping, a thick, violet paste of the required racemate is formed, which is well washed with alcohol and ether to remove oxalic acid, and may then be used for the resolution.

l-*Dichlorodiethylenediaminechromic* d-*bromocamphorsulphonate*,

$$[Cl_2Cr\,en_2]SO_3\cdot C_{10}H_{14}OBr,$$

forms small, shining, violet crystals, and has [α] = −35°, [M] = −193·55°. The corresponding d-l-*salt* has $[\alpha]_D$ = +32°, and $[M]_D$ = +176·9°. The solutions rapidly undergo racemisation. The active 1:2-*dichlorodiethylenediaminechromic chlorides*, $[Cl_2Cr\,en_2]Cl,H_2O$,

were obtained from the bromocamphorsulphonates by treatment with concentrated hydrochloric acid; they form small, violet needles. The *bromides*, $[Cl_2Cr\,en_2]Br$, were prepared from the chlorides and hydrobromic acid, and crystallise in small, reddish-violet needles. The *nitrates*, $[Cl_2Cr\,en_2]NO_3$, were obtained from the chlorides and nitric acid as violet, crystalline powders. T. S. P.

Chemico-Crystallographic Examination of the Platinichlorides, Platinibromides, Stannichlorides, and Stannibromides of Quaternary Ammonium Bases. A. RIES (*Zeitsch. Kryst. Min.*, 1911, 49, 513—617).—The quaternary ammonium bases, the salts of which have been examined, are those containing the groups NMe_4, NMe_3Et, NMe_3Pr^{α}, NMe_3Pr^{β}, NMe_2Et_2, $NMeEt_3$, $NMe_3{\cdot}C_4H_9$, $NMe_3{\cdot}CH_2Pr^{\beta}$, NMe_2EtPr^{α}, NEt_4, $NMe_3{\cdot}CH_2{\cdot}CHMeEt$, $NMe_3{\cdot}CH_2{\cdot}CH_2Pr^{\beta}$, $NMeEt_2Pr^{\alpha}$, $NMe_2Pr^{\alpha}_2$, NEt_3Pr^{α}, $NMeEtPr^{\alpha}_2$, $NMePr^{\alpha}_3$, $NEt_2Pr^{\alpha}_2$, $NEt_3{\cdot}C_4H_9$, $NEt_3{\cdot}CH_2Pr^{\beta}$, $NMeEtPr^{\alpha}{\cdot}CH_2Pr^{\beta}$, $NEtPr^{\alpha}_3$, NPr^{α}_4, $NPr^{\alpha}_3{\cdot}CH_2Pr^{\beta}$, $NMe(CH_2Pr^{\beta})_3$, $NEt(CH_2Pr^{\beta})_3$, $NPr^{\alpha}(CH_2Pr^{\beta})_3$, and $N(CH_2Pr^{\beta})_4$. The crystallographic properties of the platini-chlorides and -bromides, and stanni-chlorides and -bromides of these bases are described; their m. p.'s or points of decomposition are stated; in many cases the densities of the several modifications of any one salt have been determined by the floating method in acetylene tetrabromide and toluene, and the transition temperatures of the modifications have been ascertained.

After a detailed comparison of the preceding physical constants, the author states the following generalisations:

(1) The m. p.'s decrease, and the transition temperatures (of the several modifications) increase, as the molecular weights of the tetra-alkylammonium platinichlorides increase.

(2) In the case of two isomeric salts, the one containing one or more *iso*alkyl groups has a lower m. p. and a higher transition temperature (for corresponding modifications) than that containing normal alkyl groups.

(3) The temperatures, at which the corresponding point systems of two or more isomeric and metameric salts undergo transition into the more highly symmetric analogous point systems, are higher the less is the symmetry of the molecule corresponding with the point system.

(4) The region of stability of the different modifications is dependent on the molecular weight and the symmetry of the molecule.

Experiments on the morphotropic relations of the salts with regard to their topic axis show that the platinichloride, platinibromide, and stannichloride of a given tetra-alkylammonium base form isomorphous mixtures in all proportions.

An outstanding feature of the author's experiments is the regular shifting at high temperatures of the region of stability of the polymorphous modifications of members of homologous series. The paper concludes with a discussion of the question whether this regularity is characteristic of all salts of members of the families in the periodic table. A consideration of the transition temperatures of the modifi-

cations of the nitrates of the alkali metals, of the halides of mercury, of the carbonates of the magnesium-barium group and so forth, indicates that the answer to the question is in the affirmative.

C. S.

Methylated Polypeptides. Betaine of Diglycylglycine. EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1911, 75, 19—29. Compare this vol., i, 528).—*Trimethyldiglycylglycine*, $OH\cdot NMe_3\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$ or

$$NH{<}\begin{matrix}CO\cdot CH_2\cdot NMe_3{-}O\\ CH_2\cdot CO\cdot NH\cdot CH_2\end{matrix}{>}CO,$$

obtained from chloroacetylglycylglycine and trimethylamine, is isolated in the form of the *platinichloride*, which forms orange-yellow, prismatic crystals, m. p. 181° (corr., decomp.).

The *ethyl* ester, prepared by decomposition of the platinichloride with hydrogen sulphide and treatment of the hydrogen chloride of the base with ethyl alcohol and hydrogen chloride, yields a *platinichloride*, crystallising in slender, lustrous, bright orange-yellow plates. The *platinichloride* of the corresponding *methyl* ester, prepared in the same way, crystallises in six-sided prisms, m. p. 180°. Analysis showed it to be partly hydrolytically decomposed. When prepared by dissolving the platinichloride of the base in methyl alcohol and saturating with dry hydrogen chloride, it was obtained in yellow needles, m. p. 215·5—216·5° (corr., decomp.).

Trimethyldiglycylglycine when hydrolysed with boiling concentrated hydrochloric acid for fifteen hours gives betaine hydrochloride and glycine hydrochloride, the resolution being complete. Trimethyl-*dl*-leucylglycine when boiled for two hours with fuming hydrochloric acid is recovered almost unchanged.

Hydrolysis leading to the formation of betaine took place on attempting to methylate chloroacetylalanine with trimethylamine, and a similar behaviour was shown by chloroacetyl-*l*-tyrosine. Betaine was obtained further on attempting to methylate glycylglycine with methyl iodide. When attempting to methylate polypeptides with methyl iodide and potassium hydroxide, products containing iodine and potassium were usually obtained; these probably represent potassium iodide additive products.

E. F. A.

Preparation of Iodo-fatty Acid Compounds and their Behaviour in the Animal. EMIL ABDERHALDEN and PAUL HIRSCH [and M. GUGGENHEIM] (*Zeitsch. physiol. Chem.*, 1911, 75, 38—56).—*Iodoacetylglycine*, $CH_2I\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, prepared by the reaction of glycine with iodoacetyl chloride in *N*-sodium hydroxide, sinters at 130°, and begins to melt at 142°, m. p. 160°, decomp. 165°.

dl-*a-Iodopropionylglycine*, $CHMeI\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, from glycine and a-iodopropionyl chloride, sinters and begins to melt at 60°, m. p. 80°, decomp. 135°. The *ethyl* ester crystallises in needles, which sinter at 45°, m. p. 60°, and give up iodine at 225°. dl-*a-Iodopropionyl*-dl-*alanine*, $CHMeI\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, crystallises in needles, which sinter at 155°, m. p. 180—190°, decomp. 194°. The *ethyl* ester forms yellow needles, which sinter at 50°, m. p. 52—60°, decomp. 234° with liberation of iodine.

Di-iodoelaidyl chloride, $C_{17}H_{33}I_2 \cdot COCl$, is obtained as a brownish-red mass by the action of thionyl chloride on di-iodoelaidic acid. With glycine, *di-iodoelaidylglycine*, $C_{17}H_{33}I_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, is obtained. The amorphous, colourless product sinters at 52°, m. p. 57°. The *ethyl* ester, prepared by interaction of the chloride with glycine ester, is crystalline, m. p. 82°, after sintering at 70°.

Di-iodoelaidylalanine sinters at 54°, m. p. 64°; it has $[\alpha]_D^{20}$ $-4 \cdot 9°$. The corresponding ester was only obtained as a syrup.

Di-iodoelaidyl-di-iodotyrosine,

$$C_{17}H_{33}I_2 \cdot CO \cdot NH \cdot CH(CH_2 \cdot C_6H_2I_2 \cdot OH) \cdot CO_2H,$$

sinters at 92°, m. p. 170°.

Iodobehenyl chloride, $C_{21}H_{42}I \cdot COCl$, from iodobehenic acid and thionyl chloride, could not be distilled. It couples readily with amino-acids. *Iodobehenylglycine* is an amorphous, faintly yellow-coloured, fatty mass; it sinters at 50°, m. p. 70°, decomp. 170—180°.

Ethyl di-iodobrassidate (lipoiodin), $C_8H_{17} \cdot CHI \cdot CHI \cdot C_{11}H_{22} \cdot CO_2Et$, sinters at 32°, m. p. 40°, decomp. 220—230°, liberating iodine.

The physiological experiments indicate that iodine administered as di-iodoelaidic acid is slowly but completely excreted. The iodine of di-iodoelaidylglycine was in ten days only 50% excreted. The resorption was complete, but in the case of the ethyl ester it was less complete. Most of the iodine is in the fæces; in some experiments none was present in the urine.

Di-iodo-*l* tyrosine and di-iodoelaidyl-*l*-tyrosine are badly resorbed; ethyl di-iodobrassidate is better resorbed. E. F. A.

α-Aminobutyric Acid. EMIL ABDERHALDEN (*Zeitsch. physiol.*, 1911, **74**, 509—510).—Polemical. Koelker (this vol., i, 773) has not mentioned that Abderhalden, Chang, and Wurm (this vol., i, 526) have previously studied the behaviour of *dl*-α-aminobutyric acid towards yeast. E. F. A.

Alkylation of Commercial Cyanamide Salts. WILHELM TRAUBE and ALFRED ENGELHARDT (*Ber.*, 1911, **44**, 3149—3152. Compare Traube and Wedelstaedt, Abstr., 1900, i, 389).—The relatively pure disodium cyanamide, and likewise the crude commercial calcium cyanamide, react very readily with halogen alkyl and with dialkyl sulphate in presence of water or alcohol, forming disubstituted cyanamides. These are converted into secondary amines without difficulty, and it is easy to separate the ammonia formed at the same time. This affords a very convenient method of preparing secondary amines in quantity. Dimethyl-, diethyl-, di-*iso*amyl-, and dibenzyl cyanamide have been prepared in the manner described: from calcium cyanamide and methyl sulphate, 70—80% of the theoretical quantity of dimethylamine is obtained. Dimethylcyanamide has b. p. 163·5° (corr.); *diethylcyanamide*, b. p. 78°/16 mm.; *di-*iso*amylcyanamide*, b. p. 134°/14 mm.; *dibenzylcyanamide* forms transparent, rhombic plates, m. p. 53·5° (corr.). E. F. A.

Acylation and Alkylation of Cyanamide. OTTO DIELS and RICHARD GOLLMANN (*Ber.*, 1911, **44**, 3158—3165).—Cyanamide can

be acylated with ethyl chlorocarboxylate by the Schotten-Baumann method without difficulty, ethyl cyaniminodicarboxylate,

$$NC\cdot N(CO_2Et)_2,$$

being formed. With phosphoric oxide, the formation of cyano*iso*cyanate [carbimidonitrile] was expected; actually carbethoxyl *iso*cyanate [ethyl carbimidecarboxylate], $CO\colon N\cdot CO_2Et$, is formed, identical with the substance prepared by Diels and Wolf (Abstr., 1906, i, 237) by the action of phosphoric oxide on ethyl nitrogentricarboxylate.

Ammonia converts the diacylated cyanamide into the crystalline ammonium salt of the monoacyl compound, $NC\cdot N(NH_4)\cdot CO_2Et$. Dilute acids form ethyl allophanate; concentrated acids cause the addition of water and the formation of ethyl *as*-carbamidedicarboxylate,

$$NH_2\cdot CO\cdot N(CO_2Et)_2.$$

By the interaction of methyl sulphate and cyanamide, the monomethylcyanamide initially formed is polymerised to iso*trimethylmelamine*, $NH<\begin{matrix}C(\colon NMe)\cdot NH\\ C(\colon NMe)\cdot NH\end{matrix}>C\colon NMe$, but dimethylcyanamide is very readily obtained in this manner. It is easily converted into dimethylcarbamide.

Ethyl cyanoiminodicarboxylate, $NC\cdot N(CO_2Et)_2$, forms long, lustrous, silky prisms, with a burning taste, m. p. 33° (Bässler, Abstr., 1878, 214).

Methyl cyanoiminodicarboxylate, $NC\cdot N(CO_2Me)_2$, crystallises in lustrous, octahedra, m. p. 96—97°.

Ethyl carbimidecarboxylate (Diels and Wolf, *loc. cit.*) is a transparent, mobile liquid, b. p. 115—116°/781 mm.

Methyl carbimidecarboxylate, $CO\colon N\cdot CO_2Me$, is a transparent, mobile liquid of intensely biting odour, b. p. 97—98°; it decomposes on keeping to a colourless, crystalline compound, probably a polymeride.

Methyl phenylallophanate, $NHPh\cdot CO\cdot NH\cdot CO_2Me$, prepared by the interaction of methyl carbamidecarboxylate with aniline, crystallises in long needles, m. p. 143—144°.

The *ammonium* salt of *ethyl cyaniminocarboxylate*,

$$CN\cdot N(NH_4)\cdot CO_2Et,$$

forms lustrous, compact, octahedral crystals, m. p. 107—108°.

Ethyl as-*carbamidedicarboxylate*, $NH_2\cdot CO\cdot N(CO_2Et)_2$, crystallises in lustrous prisms, m. p. 86—87°, of faintly sweet taste. The corresponding *methyl* ester separates in slender, colourless needles, m. p. 137—138° (decomp.).

Dimethylcyanamide has b. p. 52°/14 mm.

as-*Dimethylcarbamide*, $NH_2\cdot CO\cdot NMe_2$, forms large, compact, lustrous prisms, m. p. 181—182°; it tastes sweet. E. F. A.

Synthesis of δ-Guanidinovaleric Acid. DANKWART ACKERMANN, R. ENGELAND, and FRIEDRICH KUTSCHER (*Zeitsch. Biol.*, 1911, 57, 179—182).—δ-Aminovaleric acid and cyanamide were set aside in concentrated aqueous solution for some weeks, when a crystalline crust of *δ-guanidonovaleric acid*, $CO_2H\cdot[CH_2]_4\cdot NH\cdot C(NH_2)\colon NH$, separated. This forms short, stunted, hard crystals, m. p. 265—266°, after previously becoming brown and sintering. When evaporated

with concentrated hydrochloric acid, the *chloride* is obtained in long, lustrous needles, m. p. 170—171°. The *aurichloride* forms broad, lustrous plates, m. p. 120—122°. The *platinichloride* is very soluble and not characteristic. E. F. A.

Hypobromous [Acid and] Amides. ÉTIENNE BOISMENU (*Compt. rend.*, 1911, **153**, 678—680. Compare François, Abstr., 1909, i, 13, 140).—A description of the preparation of certain bromo-amides by the action of hypobromous acid on the amides.

Bromoformamide, H·CO·NHBr, is best prepared by the action of bromine on a solution of formamide in ethyl acetate in presence of silver oxide. It is thus obtained in crystals, m. p. 87—88° (decomp.). W. O. W.

A New Derivative of Carbamide, Chlorocarbamide. AUGUSTE BÉHAL and A. DETŒUF (*Compt. rend.*, 1911, **153**, 681—683. Compare Chattaway, Trans., 1909, **95**, 464).—Carbamide absorbs chlorine at 15°, forming a mixture of monochlorocarbamide and carbamide hydrochloride. The former may be isolated in a state of purity by adding carbamide (60 grams) to water (13 grams), cooling in ice, and passing chlorine until the weight increases by 32 grams. The clear liquid is cooled in methyl chloride for thirty minutes, the chlorocarbamide filtered in a vacuum, and washed with a previously prepared solution of the same substance.

Chlorocarbamide, NH_2·CO·NHCl, occurs in crystals, m. p. 71° (decomp.). It is soluble in five parts of water at the ordinary temperature, giving a neutral solution which slowly loses nitrogen, at the same time becoming acid and forming biuret. The substance behaves towards saturated organic compounds as a chlorinating or as an oxidising agent, or sometimes as hypochlorous acid, forming additive compounds. With unsaturated substances, it effects addition of hypochlorous acid or of chlorocarbamide, but sometimes brings about oxidation. The reactions are progressive, and their course can be followed by titration. W. O. W.

Ethyl Azodicarboxylate. OTTO DIELS and PAUL FRITZSCHE (*Ber* 1911, **44**, 3018—3027).—Ethyl azodicarboxylate reacts normally with piperidine in cold petroleum, yielding the *dipiperidide*,

$$N_2[CO\cdot C_5NH_{10}]_2,$$

m. p. 134—135° (decomp.), golden-yellow prisms, but forms with aniline an additive *compound*, $C_{12}H_{17}O_4N_3$, m. p. 138°, of unknown constitution, although probably it is a hydrazine derivative, since it crystallises in colourless plates and prisms. A similar colourless *compound*, $C_{14}H_{21}O_4N_3$, m. p. 75—76°, is obtained with dimethylaniline.

Acting as a mild oxidising agent in consequence of its tendency to yield ethyl hydrazinedicarboxylate, ethyl azodicarboxylate very smoothly converts quinol into *p*-benzoquinone.

Reacting in methyl-alcoholic solution at 0°, hydrazine hydrate and methyl chlorocarbonate yield hydrazine hydrochloride and *methyl hydrazinecarboxylate hydrochloride*, $CO_2Me\cdot NH\cdot NH_2,HCl$, m. p. 160°.

The *base*, $C_2H_6O_2N_2$, m. p. 63°, b. p. 108°/12 mm, colourless prisms, has a faint, alkaline reaction, is volatile with steam, yields a *benzylidene* derivative, $CO_2Me\cdot NH\cdot N:CHPh$, m. p. 146°, and with aqueous potassium cyanate at 0°, the *semicarbazide*, $CO_2Me\cdot NH\cdot NH\cdot CO\cdot NH_2$, m. p. 169—170°, and reacts with methyl chlorocarbonate in ether to form *methyl hydrazinedicarboxylate*, $CO_2Me\cdot NH\cdot NH\cdot CO_2Me$, m. p. 131°. This ester, which is very stable and resists the attack of strong acids or bases, is also formed by the action of warm aqueous potassium hydroxide on methyl hydrazinecarboxylate hydrochloride. *Methyl azodicarboxylate*, $N_2[CO_2Me]_2$, b. p. 96°/25 mm., is prepared by the action of fuming nitric acid on methyl hydrazinedicarboxylate in nitric acid, D 1·4, at 0°, and behaves like the ethyl ester. C. S.

Dehydrogenation by Catalysis. NICOLAI D. ZELINSKY (*Ber.*, 1911, **44**, 3121—3125; *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1220—1222).—Heated palladium black, prepared by reducing ammonium palladochloride by means of formic acid in presence of alkali, serves as an excellent catalyst for the dehydrogenation of *cyclo*hexane and methyl*cyclo*hexane, which lose all the six hydrogen atoms of the ring and yield hydrogen and benzene or toluene, with no trace of the tetrahydro- or dihydro-derivative of the aromatic hydrocarbon. This action commences at about 170°, and proceeds very rapidly at 200—300°.

At lower temperatures, the reverse change occurs, passage of hydrogen and benzene over the freshly-prepared palladium black heated at 100—110° resulting in the hydrogenation of the benzene. Under these conditions, the temperature of equilibrium is about 200°, since, above this temperature, in spite of the presence of excess of hydrogen, dehydrogenation occurs.

The catalytic decomposition of *cyclo*hexane hydrocarbons under the influence of palladium seems to be specific, as neither hexane, nor *cyclo*pentane, nor methyl*cyclo*pentane undergoes similar dehydrogenation, at any rate below 300°. This reaction hence serves to distinguish between five- and six-carbon atom rings. T. H. P.

Selective Catalysis: A New Tetrahydrobenzene [*cyclo*Hexene]. NICOLAI D. ZELINSKY (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1222—1224).—Dehydrogenation of *cyclo*hexene (prepared by the action of oxalic acid on *cyclo*hexanol) under the influence of palladium proceeds more energetically than that of *cyclo*hexane (compare preceding abstract), the products being hydrogen and benzene. The *cyclo*hexene employed in this experiment showed a continuous absorption spectrum, whilst another preparation, obtained by the action of quinoline on iodo*cyclo*hexane, was found to exhibit more or less marked selective absorption. The latter *cyclo*hexene only underwent partial dehydrogenation in presence of palladium, the benzene formed being mixed with a new *cyclo*hexene, C_6H_{10}, b. p. 77·5—78° (corr.), D_4^{20} 0·8005, n_D^{20} 1·4416, the increment of the molecular refraction being 1·58; it has a fatty, aromatic odour, and is a saturated hydrocarbon, as it reacts with neither permanganate nor bromine. T. H. P.

Isomerisation of Unsaturated Cyclic Hydrocarbons, C_8H_{12}. (Mlle.) V. I. Egorova (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1116—1124).—*cyclo*Hexylacetylene, $C_6H_{11}\cdot C\vdots CH$, best prepared by the method of Darzens and Rost (Abstr., 1909, i, 899), has D_0^0 0·8602, D_0^{20} 0·8424, n_D^{20} 1·4597.

cyclo*Hexylidene-ethylene*, $CH_2\colon C\colon C_6H_{10}$, obtained on heating *cyclo*hexylacetylene with alcoholic potassium hydroxide for ten hours at 140°, is a liquid, b. p. 138—141°, D_0^0 0·8682, D_0^{20} 0·8508, n_D 1·4826, and, when heated with sodium in a sealed tube, gives the sodium derivative of *cyclo*hexylacetylene (Darzens and Rost, *loc. cit.*).

1-*Vinyl*-Δ^1-cyclo*hexene*, $CH_2\colon CH\cdot C\lessdot\begin{matrix}CH_2\cdot CH_2\\CH-CH_2\end{matrix}\gtrdot CH_2$, prepared by heating *cyclo*hexylidene-ethylene with benzoic acid in a sealed tube for ten hours at 170°, is a liquid, b. p. 143—145°, D_0^0 0·8862, D_0^{20} 0·8701, n_D^{20} 1·49060, and, although it contains a conjugated linking, shows no optical exaltation (compare Auwers and Eisenlohr, Abstr., 1910, ii, 365); it does not react with sodium. T. H. P.

Polymerisation of Diethylene Hydrocarbons. III. Divinyl. Sergius V. Lebedeff and (Mlle.) N. A. Skavronskaja (*J Russ. Phys. Chem. Soc.*, 1911, 43, 1124—1131).—This paper is largely a repetition of one already published (this vol., i, 26).

4-Ethenyl*cyclo*-Δ^1-hexene (*loc. cit.*) gives with bromine 1-*αβ-dibromoethyl*-3 : 4-*dibromo*cyclo*hexane*,

$$CHBr\lessdot\begin{matrix}CH_2-CH_2\\CHBr\cdot CH_2\end{matrix}\gtrdot CH\cdot CHBr\cdot CH_2Br,$$

m. p. 69·5—70·5°. When oxidised with permanganate it yields β-carboxyadipic acid (butane-αβδ-tricarboxylic acid), m. p. 111—113° (compare Guthzeit and Engelmann, Abstr., 1902, i, 742; Leuchs and Möbis, Abstr., 1909, i, 361).

The polymeride obtained, together with the above dimeride, on heating divinyl, yields an ozonide (*loc. cit.*) identical with that given by di*cyclo*octadiene (compare Harries, Abstr., 1908, i, 254). The conclusion is hence drawn that the polymeride has the structure $\left(\begin{matrix}CH_2\cdot CH\colon CH\cdot CH_2\\ | \qquad\qquad | \\CH_2\cdot CH\colon CH\cdot CH_2\end{matrix}\right)_x$, and is de-polymerised by the action of ozone.

T. H. P.

Benzene Problem. Ernst Mohr (*Ber.*, 1911, 44, 2971).—Pauly has recently suggested (this vol., i, 986) that the existence of the aromatic hydrocarbon, $C_{13}H_9$, decides for the centric formula for benzene in place of the Kekulé formula. It is doubtful, however, whether this criterion can be accepted, since the hydrocarbon, $C_{13}H_9$, does not conform with the law of even numbers of atoms, and is therefore analogous to triphenylmethyl and the radicle of diphenyl nitrogen, NPh_2, rather than with benzene, naphthalene, and anthracene.

T. A. H.

A New Hypothesis on Benzene. Aníbal Chacón (Pamphlet, pp. 43).—See this vol., ii, 1080.

[Orientation in the Benzene Nucleus.] JULIUS OBERMILLER (*Ber.*, 1911, **44**, 3179—3180).—A renewed claim for priority over Holleman (compare Abstr., 1910, i, 826; also Holleman and Caland, this vol., i, 849). E. F. A.

Oxidation of Amino-acids by Alloxan, Isatin, and *p*-Benzoquinone. WILHELM TRAUBE (*Ber.*, 1911, **44**, 3145—3148).—It was first shown by Strecker that alloxan oxidises aliphatic α-amino-acids to the aldehyde of the next lower carbon series with liberation of crabon dioxide and ammonia. Hurtley and Wootton (Trans., 1911, **99**, 288) have shown that dimethylalloxan behaves similarly. It is now found that alloxan likewise oxidises anilinoacetic acid to benzaldehyde and carbon dioxide, the solution becoming red. The amount of benzaldehyde produced was determined quantitatively by means of the phenylhydrazone.

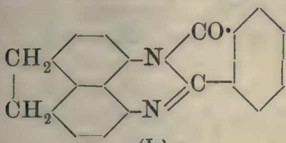
Besides alloxan, isatin, *p*-benzoquinone and toluquinone are shown to oxidise the amino-acid to aldehyde, whereas naphthaquinone and anthraquinone, parabanic acid, and chloroanil are without action. Fatty aromatic amines, for example, benzylamine, are in like manner oxidised to aldehydes by alloxan and isatin, but *p*-benzoquinone is without effect. Purely fatty amines, for example, *iso*amylamine, are not oxidised by alloxan. E. F. A.

Acenaphthene. II. FRANZ SACHS and GERHARDT MOSEBACH (*Ber.*, 1911, **44**, 2852—2862. Compare Abstr., 1910, i, 726).—The importance recently acquired by acenaphthene for technical purposes renders desirable an extension of the accurate knowledge of its substitution products. 4-Acetylaminoacenaphthene in glacial acetic acid at 0° is converted by concentrated nitric acid into 2-*nitro*-3-*acetylaminoacenaphthene*, $NHAc\cdot C_{12}H_8\cdot NO_2$, m. p. 253°, yellow needles, in which the ortho-relation of the substituents is proved by the fact that the compound in aqueous alcohol is reduced by sodium hyposulphite to the *iminoazole*, $C_{12}H_8<\begin{matrix}-N-\\NH\end{matrix}>CMe$ (*nitrate*, $C_{14}H_{12}N_2,HNO_3$, m. p. 320°; *platinichloride*, $2C_{14}H_{12}N_2,H_2PtCl_6$; *chloride*, $C_{14}H_{12}N_2,HCl$), and also by the fact that the 2-*nitro*-3-*aminoacenaphthene*, m. p. 222—224°, red prisms, obtained by its hydrolysis by alcohol and concentrated hydrochloric acid, is reduced by stannous chloride and hydrochloric acid to 2 : 3-*acenaphthylenediamine*, m. p. 140—142°, almost colourless needles, which condenses with phenanthraquinone and with diacetyl to form the *azines*, $C_{12}H_8<\begin{matrix}N\\N\end{matrix}>C_{14}H_8$, m. p. 293°, yellow needles, and $C_{12}H_8<\begin{matrix}N:CMe\\ \vert \\ N:CMe\end{matrix}$, m. p. 200°, respectively.

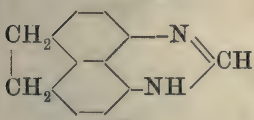
2-Nitro-3-acetylaminoacenaphthene is converted by boiling alcoholic sodium hydroxide into the *sodium* salt of 2-nitro-3-hydroxyacenaphthene, $ONa\cdot C_{12}H_8\cdot NO_2,H_2O$, dark red crystals. 2-*Nitro*-3-*hydroxyacenaphthene* itself has m. p. 148°, crystallises in yellowish-red needles, and is reduced by sodium hyposulphite in aqueous alcohol to 2-*amino*-3-*hydroxyacenaphthene*, m. p. 159°.

Quincke's 3 : 4-dinitroacenaphthene is obtained best by heating a

finely-divided suspension of acenaphthene in glacial acetic acid with concentrated nitric acid at 80° for twenty minutes. Its reduction to 3 : 4-acenaphthylenediamine is conveniently effected by an excess of stannous chloride and hydrochloric acid. The *peri*-position of the two amino-groups is proved by the preparation of the following substances.



(I.)



(II.)

Phthalo-aceperinone (formula I), m. p. 290°, red needles, from the diamine and phthalic anhydride at about 200°; *aceperimidine* (formula II), m. p. 285°, greenish-brown crystals, from the diamine and formic acid in boiling alcohol; *acenaphthylene*-3 : 4-*thiocarbamide*, $C_{12}H_8<\substack{NH \\ NH}>CS$, colourless crystals, from the diamine and carbon disulphide in alcohol. C. S.

Cholesterol. XIII. Cholesterylamine. ADOLF WINDAUS and J. ADAMLA (*Ber.*, 1911, **44**, 3051—3058).—In their attempts to prepare cholesterylamine, the authors obtained *cholesterylurethane*, $C_{27}H_{45}O \cdot CO \cdot NH_2$, m. p. 212—213°, by heating cholesterol and carbamide at 220°. *Cholesterylamine*, $C_{27}H_{45}\ NH_2$, m. p. 98°, is obtained by heating cholesteryl chloride and alcoholic ammonia at 180° in the presence of a little ammonium iodide. The *hydrochloride, sulphate, platinichloride,* and *picrate*, m. p. 274—275° (decomp.), are described. The *acetyl* and the *benzoyl* derivatives have m. p. 243—244° and 236° respectively. The reduction of cholestenoneoxime by sodium and boiling alcohol yields a mixture of stereoisomeric bases (*picrate*, decomp. 253°; *platinichloride*, decomp. 252°; *benzoyl* derivative, m. p. 203°). The acetylated mixture has been separated by fractionation into three individual substances; one, identical with the preceding acetyl derivative, has m. p. 243—244°, another, *β-acetylcholesterylamine*, has m. p. 216—217°, and constitutes the chief ingredient of the acetylated mixture, whilst the third, *γ-acetylcholesterylamine*, has m. p. 190°.

C. S.

Synthesis of Aromatic and Hydroaromatic Alcohols Containing the Allyl Group. IPPOLYT MATSCHUREVITSCH (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 973—990).—The author has prepared a number of tertiary alcohols by the interaction of allyl bromide (or iodide), magnesium, and a carbonyl compound in ethereal solution (compare Javorsky, Abstr., 1908, i, 753).

o-4-*Xylylmethylallylcarbinol*, $C_6H_3Me_2 \cdot CMe(OH) \cdot CH_2 \cdot CH{:}CH_2$, prepared from *o*-4-xylyl methyl ketone, allyl bromide, and magnesium, is a colourless, viscous liquid with an aromatic odour, b. p. 144—144·5°/19·5 mm., $D_4^{21\cdot5}$ 0·97258, $n_D^{21\cdot5}$ 1·52752.

m-4-*Xylylmethylallylcarbinol*, prepared from *m*-4-xylyl methyl ketone, is a pleasant-smelling, colourless, viscous liquid, b. p. 139—139·5°/14·5 mm., $D_4^{21\cdot5}$ 0·97675, $n_D^{21\cdot5}$ 1·52882.

p-2-*Xylylmethylallylcarbinol*, prepared from *p*-2-xylyl methyl

ketone, is a liquid, b. p. 138—139°/22·5 mm., $D_4^{21\cdot5}$ 0·97774, $n_D^{21\cdot5}$ 1·52925.

1-*Allyl*cyclo*hexane*-1-*ol*, $OH\cdot C_6H_{10}\cdot CH_2\cdot CH\colon CH_2$, prepared from *cyclo*hexanone, is a liquid, b. p. 95—97°/27·5 mm., D_4^{22} 0·93410, n_D^{22} 1·47564.

1-*Methyl*-3-*allyl*-Δ^1-cyclo*hexene*-3-*ol*,

$$CH_2<\begin{matrix}CMe\colon CH\\ CH_2\cdot CH_2\end{matrix}>C(OH)\cdot CH_2\cdot CH\colon CH_2,$$

prepared from 1-methyl-Δ^1-*cyclo*hexene-3-one, is a liquid, b. p. 99·5—100°/16·5 mm., D_4^{22} 0·95510, n_D^{22} 1·49923.

1 : 3-*Dimethyl*-5-*allyl*-Δ^3-cyclo*hexene*-5-*ol*,

$$OH\cdot C_6H_6Me_2\cdot CH_2\cdot CH\colon CH_2,$$

prepared from 1 : 3-dimethyl-Δ^3-*cyclo*hexene-5-one, forms a fibrous, crystalline, fatty mass, m. p. 28—31°, b. p. 108—108·5°/17·5 mm.

1-*Methyl*-5-*ethyl*-3-*allyl*-Δ^1-cyclo*hexene*-3-*ol*,

$$OH\cdot C_6H_6MeEt\cdot CH_2\cdot CH\colon CH_2,$$

has b. p. 120—122°/13·5 mm., D_4^{22} 0·91795, n_D^{22} 1·48731.

1-*Methyl*-5-*propyl*-Δ^1-cyclo*hexene*-3-*one*, $CHPr<\begin{matrix}CH_2-CO\\ CH_2\cdot CMe\end{matrix}\geqslant CH$, obtained by condensing ethyl acetoacetate and *n*-butaldehyde in presence of diethylamine to ethyl $\alpha\gamma$-diacetyl-β-propylglutarate, $CO_2Et\cdot CHAc\cdot CHPr^{\alpha}\cdot CHAc\cdot CO_2Et$, and treating the latter with alkali, is a colourless liquid, b. p. 242—244°, 128—129°/37 mm., $D_4^{22\cdot5}$ 0·9267.

1-*Methyl*-5-*propyl*-3-*allyl*-Δ^1-cyclo*hexene*-3-*ol*,

$$CH_2<\begin{matrix}CMe=\!=CH\\ CHPr^{\alpha}\cdot CH_2\end{matrix}>C(OH)\cdot CH_2\cdot CH\colon CH_2,$$

prepared from the preceding compound, is a crystalline, waxy mass, m. p. 34—37°, b. p. 135—136°/29 mm., $D_4^{22\cdot5}$ 0·9225.

1-*Methyl*-5-iso*propyl*-3-*allyl*-Δ^1-cyclo*hexene*-3-*ol*, $C_{13}H_{22}O$, forms a waxy mass, m. p. 26—29°, b. p. 127—128°/25·5 mm., $D_4^{22\cdot5}$ 0·9175, $n_D^{22\cdot5}$ 1·48905.

1-*Methyl*-5-iso*butyl*-3-*allyl*-Δ^1-cyclo*hexene*-3-*ol*, $C_{14}H_{24}O$, prepared from the corresponding hexenone, was obtained as a crystalline, waxy mass, m. p. 50—52·5°, b. p. 140—142°/38 mm. T. H. P.

Bromination of Phenol. J. G. Dinwiddie and Joseph H. Kastle (*Amer. Chem. J.*, 1911, 46, 502—503).—It is well known that when bromine is added to an aqueous solution of phenol, tribromophenol and tribromophenol bromide are the only compounds produced. It is now shown that if bromine is added to solutions of phenol in glacial acetic acid, chloroform, carbon tetrachloride, or carbon disulphide, substitution takes place with the formation of a dibromophenol, probably the 2 : 4-derivative.

It is suggested that the peculiar behaviour of phenol in aqueous solution is due to its tendency to form quinonoid derivatives. Tribromophenol bromide, $CO<\begin{matrix}CBr\colon CH\\ CBr\colon CH\end{matrix}>CBr_2$, is first produced, and reacts with phenol to form 2 : 4 : 6-tribromophenol. The mechanism of these reactions is discussed. E. G.

Isomerism and Polymorphism. II. EINAR BIILMANN (*Ber.*, 1911, **44**, 3152—3157).—Polemical (compare Hantzsch, Abstr., 1910, i, 474; this vol., i, 715; Biilmann, this vol., i, 367).

Hantzsch's contention as to the persistence of the individuality of the homochromoisomerides is based on what is probably only a retention of the inoculation nuclei.

Polymorphism is a very general property. Methylcoumarinic acid has been obtained in a new modification, m. p. 86°, in addition to that, m. p. 91—92°. E. F. A.

The Reactivity of Benzene Substituents and the Acidity of Aromatic Acids in their Dependence on Orientating Influences. The Structure of Benzene. JULIUS OBERMILLER (*J. pr. Chem.*, 1911, [ii], **84**, 449—459). The author finds that the removal of the sulphoxyl group from *o*-phenolsulphonic acid by heating with hydrochloric acid at 100°, takes place more readily than with the para-compound, whilst the meta-acid, when subjected to the same treatment, remains intact.

The mobility of the sulphoxyl group thus increases as the latter approaches the hydroxyl group, as represented in Claus's diagonal formula for benzene. The view is expressed that the increase in the reactivity of the hydrogen atoms of a side-chain is coincident with an increase in its acid character. The acidity of the side-chain should accordingly be greater the less firmly it is attached, and with position-isomeric compounds increase in the order meta, para, ortho. This is confirmed by the behaviour of the sulphanilic acids and, to some extent, by the phenolsulphonic acids.

It is shown that the acidity of the hydroxyl group of the isomeric phenolsulphonic acids, as judged by the ease with which the dimagnesium salts are hydrolysed, diminishes in the order ortho, para, meta, whereas from measurements of the hydrogen ion concentration of the sodium salts the order of acidity is meta, para, ortho. This discrepancy is referred by the author to differences in the condition of the benzene ring. F. B.

Reactivity of Aromatic Bromo-compounds. II. Formation of Aromatic Disulphides of the Types R·S·R′·S·R and R·S·R′·S·R″. ÉDOUARD BOURGEOIS and A. FOUASSIN (*Bull. Soc. chim.*, 1911, [iv], **9**, 938—944. Compare Abstr., 1896, i, 17).—When *p*-dibromobenzene reacts with lead derivatives of the thiophenols, the two reactions represented by the following equations occur: (1) $2C_6H_4Br_2 + PbS_2R_2 = PbBr_2 + 2Br{\cdot}C_6H_4{\cdot}SR$, (2) $2Br{\cdot}C_6H_4{\cdot}SR + PbS_2R_2 = PbBr_2 + 2RS{\cdot}C_6H_4{\cdot}SR$. The first of these reactions takes place more rapidly than the second, and even if dibromobenzene is employed in large excess, some disulphide is always formed. The velocity of the second reaction increases with greater complexity of the thiophenol employed. Reaction begins at 180—185°, but only becomes practicable at 200°. Above 225° secondary actions occur. The two substances were heated together in an autoclave at 225°, and the resulting products extracted with ether or carbon disulphide and,

after removal of the solvent, fractionally distilled to separate the bromosulphide from the disulphide.

p-Bromodiphenyl sulphide (*loc. cit.*) reacts with the lead derivative of thiophenol to form *diphenyl* p-*phenylene disulphide*, $C_6H_4(SPh)_2$, m. p. 81·5°, b. p. 265°/14 mm., which crystallises in colourless spangles from hot alcohol.

p-*Bromophenyl* p-*tolyl sulphide*, $C_6H_4Br{\cdot}S{\cdot}C_6H_4Me$, m. p. 82·5°, b. p. 200·5°/14 mm., crystallises in pearly leaflets. *Di*-p-*tolyl* p-*phenylene disulphide*, $C_6H_4Me{\cdot}S{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_4Me$, m. p. 99°, b. p. 285°/14 mm., crystallises in prismatic needles.

p-*Bromophenyl α-naphthyl sulphide*, m. p. 73°, b. p. 247°, forms large, prismatic needles. *Di-α-naphthyl* p-*phenylene disulphide*, m. p. 148·5°, b. p. above 360°/14 mm. (decomp.), forms colourless, rhombic tablets.

p-*Bromophenyl β-naphthyl sulphide*, m. p. 114·5°, b. p. 253°/14 mm., forms rhombic crystals. *Di-β-naphthyl* p-*phenylene disulphide*, m. p. 185°, b. p. above 360°/14 mm. (decomp.), is nearly insoluble in neutral solvents.

Phenyl p-*tolyl* p-*phenylene disulphide*, m. p. 55·5°, b. p. 272°/14 mm., obtained by heating *p*-bromodiphenyl sulphide with the lead derivative of tolyl mercaptan, is colourless and crystalline. T. A. H.

Reactivity of Aromatic Bromo-compounds. III. Action of Bromonitrobenzenes on Phenylmercaptides. ÉDOUARD BOURGEOIS and P. HUBER (*Bull. Soc. chim.*, 1911, [iv], 9, 944—947). —It is known that *o*- and *p*-bromonitrobenzenes are more highly reactive than their meta-isomeride, and in confirmation of this, it is found that the two former, although they do not react with the lead derivative of thiophenol, give with the sodium derivative the corresponding nitrodiphenyl sulphides; with *m*-bromonitrobenzene, on the other hand, the nitro-group appears to undergo reduction with the formation of a red substance, m. p. 125·5°, which may be Gabriel's *m*-dibromoazobenzene (this Journ., 1877, i, 307).

4-Nitrodiphenyl sulphide, m. p. 54·4°, b. p. 240°/25 mm., or 262·5°/50 mm., or 288·2°/100 mm., forms pale yellow, prismatic needles or hexagonal tablets (Kehrmann and Bauer, Abstr., 1897, i, 27), and on oxidation gives 4-nitrodiphenylsulphone (Ullmann and Pasdermadjian, Abstr., 1901, i, 383).

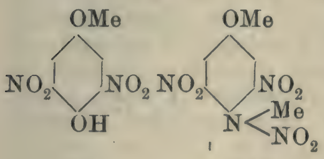
2-*Nitrodiphenyl sulphide*, m. p. 80·2°, forms pale orange-coloured crystals from alcohol mixed with ether. On oxidation it furnishes 2-nitrodiphenylsulphone (*loc. cit.*), which is colourless, but becomes brown on exposure to light. T. A. H.

The Two Forms of Decahydro-β-naphthol (a Particular Case in Stereochemistry). LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 223—227).—Leroux (Abstr., 1905, i, 278) described decahydro-β-naphthol as having m. p. 75°, b. p. 238°. Ipatieff gave m. p. 99—100°, b. p. 242—244°. By recrystallisation of a product obtained by the latter, the author has isolated two substances, A and B, which have the same composition and molecular weight, and are both stable towards permanganate. a-*Decahydro-*

β-naphthol forms flat, transparent crystals, m. p. 75°; b-*decahydro-β-naphthol* forms colourless, prismatic crystals, m. p. 103°, and is generally less soluble than its isomeride. From the consideration of the stereochemistry of monosubstituted decahydronaphthalenes it appears that four different decahydro-β-naphthols may exist, forming two pairs of enantiomorphs, and the two products above described are to be regarded as the two corresponding racemic mixtures. The stereoisomerism is due to the different positions which may be occupied by the hydrogen atoms attached to the carbon atoms 9 and 10. These two carbon atoms, although asymmetric, must necessarily have opposite configurations, and therefore the possible stereoisomerides are those due to the carbon atom to which the substituent is attached, regard being had to th edifferent situations of the two hydrogen atoms attached to the carbon atoms 9 and 10 with which a given configuration of it can be associated. R. V. S.

Constitution of Weselsky and Benedikt's Dinitroquinol Methyl Ether. Preparation of Some Methyl Derivatives of the Dinitro-*p*-anisidines. FRÉDÉRIC REVERDIN and ARMAND DE LUC (*Arch. Sci. Phys. Nat.*, 1911, [iv], 32, 343—346; *Bull. Soc. chim.*, 1911, [iv], 9, 925—928; *J. pr. Chem.*, 1911, [ii], 84, 554—558. Compare Abstr., 1881, 1139; this vol., i, 123).—The authors have determined the constitution (I) for Weselsky and Benedikt's dinitroquinol methyl ether, and (II) for a nitroamine previously described by one of them (this vol., i, 123) with m. p. 125°.

Starting with 2 : 6-dinitro-*p*-anisidine, by the action of methyl sulphate at 100°, 2 : 6-*dinitrodimethyl*-p-*anisidine*, m. p. 150°, was obtained. This substance with hot nitric acid yields a *nitroamine*, m. p. 139—140°, different from their original one; thus their *nitroamine*, m. p. 125°, is that of 3 : 5-*dinitromethyl*-p-*anisidine* (II), and since by boiling with sodium hydroxide solution it yields Weselsky and Benedikt's ether, the latter must have the constitution (I).



(I.) (II.)

The authors were unsuccessful in attempts to methylate 3 : 5-dinitro-*p*-anisidine, but succeeded in methylating the corresponding 2 : 3- and 2 : 5-compounds, which, however, unlike the 2 : 6-compound, only yielded monomethyl derivatives.

2 : 3-*Dinitromethyl*-p-*anisidine* crystallises in deep red needles, m. p. 156°.

2 : 5-*Dinitromethyl*-p-*anisidine* crystallises in dull red, felted needles, m. p. 201—202°. W. G.

Some Derivatives of Hydroxyquinol. VI. GUIDO BARGELLINI and ERMANNO MARTEGIANI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 183—190. Compare this vol., i, 305).—The present paper deals with the products of the condensation of benzoyl chloride, anisyl chloride, and phenylacetyl chloride, respectively, with hydroxyquinol trimethyl ether in the presence of aluminium chloride.

Benzoyl chloride and hydroxyquinol trimethyl ether yield a mixture of 2 : 4 : 5-trimethoxybenzophenone and 2-hydroxy-4 : 5-dimethoxybenzophenone. 2 : 4 : 5-*Trimethoxybenzophenone*, $C_{16}H_{16}O_4$, forms pale yellow needles, m. p. 97°. Its *phenylhydrazone*, $C_{22}H_{22}O_3N_2$, crystallises in colourless scales, m. p. 178—179°, and gives a yellowish-green coloration with concentrated sulphuric acid. 2-*Hydroxy*-4 : 5-*dimethoxybenzophenone*, $C_{15}H_{14}O_4$, forms yellowish-green, flat, prismatic crystals, m. p. 106—107°. Its alcoholic solution gives a yellowish-green coloration with ferric chloride. On methylation, it yields the above trimethyl ether. The *acetyl* derivative, $C_{17}H_{16}O_5$, crystallises in slightly yellow needles, m. p. 108—110°, and dissolves in concentrated sulphuric acid, giving an orange-yellow coloration. When treated with hydrobromic acid in glacial acetic acid (compare Stoermer, Abstr., 1908, i, 190), both the trimethoxy- and the dimethoxy-derivatives yield 2 : 4-*dihydroxy*-5-*methoxybenzophenone*, $C_{14}H_{12}O_4$, which forms small, yellow needles, m. p. 183—185°, and in alcoholic solution gives a yellowish-green coloration with ferric chloride. All three methoxybenzophenones dissolve in concentrated sulphuric acid with production of an orange-yellow coloration. The positions of the methoxy- and hydroxy-groups are assigned on the basis of analogies and regularities to be found in the literature, and the constitutions of the following substances are arrived at in a similar manner.

Anisyl chloride and hydroxyquinol trimethyl ether give a mixture of 2 : 4 : 5 : 4′-tetramethoxybenzophenone and 2-hydroxy-4 : 5 : 4′-trimethoxybenzophenone. 2 : 4 : 5 : 4′-*Tetramethoxybenzophenone*, $C_{17}H_{18}O_5$, is a yellowish-white, crystalline powder, m. p. 122—124°, and gives an orange-yellow coloration with sulphuric acid. Its *phenylhydrazone*, $C_{23}H_{24}O_4N_2$, has m. p. 173—174°, and dissolves in concentrated sulphuric acid, with production of a green coloration. 2-*Hydroxy*-4 : 5 : 4′-*trimethoxybenzophenone*, $C_{16}H_{16}O_5$, crystallises in small, yellow needles, m. p. 127—128°, and dissolves in concentrated sulphuric acid, producing an orange coloration. The alcoholic solution gives a yellowish-green coloration with ferric chloride.

The products of the reaction between phenylacetyl chloride and hydroxyquinol trimethyl ether are 2 : 4 : 5-trimethoxy- and 2-hydroxy-4 : 5-dimethoxy-deoxybenzoin. 2 : 4 : 5-*Trimethoxydeoxybenzoin*, $C_{17}H_{18}O_4$, crystallises in colourless leaves, m. p. 76—77°, and gives an orange coloration when dissolved in concentrated sulphuric acid. Its *phenylhydrazone*, $C_{23}H_{24}O_3N_2$, is a yellow, crystalline powder, m. p. 142—143°; it gives a yellowish-green coloration with concentrated sulphuric acid. 2-*Hydroxy*-4 : 5-*dimethoxydeoxybenzoin*, $C_{16}H_{16}O_4$, forms colourless leaves, m. p. 94°; it dissolves in concentrated sulphuric acid with production of a yellowish-green coloration, and its alcoholic solution gives a green coloration with ferric chloride. R. V. S.

Benzyl Orthothioformate. JOHN A. SMYTHE (*Proc. Univ. Durham Phil. Soc.*, 1911, 4, 75—83. Compare Dennstedt, Abstr., 1879, 318; 1880, 646).—A white, crystalline solid, m. p. 103°, produced in small quantities when hydrogen chloride acts on benzyl mercaptan in the

presence of glacial acetic acid, is proved to be identical with Dennstedt's benzyl orthothioformate. Its formation is due to the presence of formic acid as an impurity in the acetic acid employed; the yield is equivalent to the amount of formic acid present. This indicates a ready method of preparing the thio-ester by the action of hydrogen chloride on an solution of benzyl mercaptan (1 mol.) dissolved in glacial acetic acid containing sodium formate (3 mols.). The reaction under these conditions is reversible:

$$H\cdot CO_2H + 3CH_2Ph\cdot SH \rightleftharpoons CH(S\cdot CH_2Ph)_3 + 2H_2O.$$

The thio-ester can be accurately estimated by means of standard iodine solution under certain conditions. The reaction takes place in two stages; in the first, hydrochloric acid acts as a catalyst. The second stage, although reversible, proceeds almost completely, as the velocity of reaction is very great.

$$CH(S\cdot CH_2Ph)_3 + 2H_2O \rightleftharpoons H\cdot CO_2H + 3CH_2Ph\cdot SH,$$
$$2CH_2Ph\cdot SH + I_2 \rightleftharpoons (C_6H_5\cdot CH_2)_2S_2 + 2HI.$$

W. G.

Transformations of *cyclo*Butyldiethylcarbinol. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1149—1157).—As it has been found that all the transformations of *cyclo*butyldimethylcarbinol are accompanied by isomerisation of the four-membered into a five-membered ring, it is necessary to reconsider the transformations undergone by *cyclo*butyldiethylcarbinol (compare Kijner and Amosoff, Abstr., 1905, i, 772). If, with the latter, the changes are similar to those occurring with the former, the action of oxalic acid on *cyclo*butyldiethylcarbinol should give 1 : 2-diethyl-Δ^1-*cyclo*pentene, whilst the action of alcoholic potassium hydroxide on the iodo- or bromo-derivative corresponding with the alcohol should yield 1 : 1-diethyl-Δ^2-*cyclo*pentene. In the latter case it is, indeed, found that the resulting product is an unsaturated hydrocarbon, C_9H_{16}, which differs from that given with oxalic acid, and yields oxidation products in complete agreement with the conclusion that it is 1 : 1-diethyl-Δ^2-*cyclo*pentene. It is hence to be assumed that the action of hydrobromic (or hydriodic) acid on the alcohol is accompanied by isomeric change of the carbon ring, and so gives rise to 1 : 1-diethyl-2-bromo*cyclo*pentane.

[With W. AMOSOFF.]—1 : 2-*Diethyl*-Δ^1-cyclo*pentene*, $CH_2<\begin{matrix}CH_2\cdot CEt\\ \| \\ CH_2\cdot CEt\end{matrix}$, formed by the action of oxalic acid on *cyclo*butyldiethylcarbinol and previously given as $CH_2<\begin{matrix}CH_2\\ CH_2\end{matrix}>C:CEt$ (*loc. cit.*), has b. p. 151·5—152°/774 mm., and is also obtained as a by-product in the synthesis of the carbinol itself. In the reaction with oxalic acid there is no isomeric change of the tertiary into secondary alcohol, such as occurs with *cyclo*butyldimethylcarbinol. Reduction of this hydrocarbon with concentrated sulphuric acid yields (1) a saturated hydrocarbon, C_9H_{18} (*loc. cit.*), isomeric with that obtained by reducing *cyclo*butyldiethylcarbinol with hydriodic acid, and (2) an unsaturated *dimeride* of 1 : 2-diethyl-Δ^1-*cyclo*pentene, $C_{18}H_{32}$, b. p. 295—300°, or 168—173°/15 mm.

The two hydrocarbons of the formula C_9H_{18} have probably the structures:

$$CH_2{<}\begin{matrix}CH_2\cdot CHEt \\ | \\ CH_2\cdot CHEt\end{matrix} \quad \text{and} \quad CH_2{<}\begin{matrix}CHEt\cdot CH_2 \\ | \\ CHEt\cdot CH_2\end{matrix}.$$

[With S. Voznesensky.]—1 : 1-*Diethyl*-Δ^2-cyclo*pentene*,

$$CEt_2{<}\begin{matrix}CH{=}CH \\ | \\ CH_2\cdot CH_2\end{matrix},$$

has b. p. 143·5—144·5°/754 mm., D_0^{20} 0·8084, n_D 1·4455, and gives a green coloration with concentrated sulphuric acid and alcohol. On oxidation with permanganate, it yields an *acid*, $C_9H_{16}O_4$, which crystallises from light petroleum in needles, m. p. 85°, and forms an *anhydride*, $C_7H_{14}{<}\begin{matrix}CO\\CO\end{matrix}{>}O$, m. p. 10—11°, D_4^{20} 1·1077, n_D 1·4689, an *anilido-acid*, $CO_2H\cdot C_7H_{14}\cdot CO\cdot NHPh$, crystallising from aqueous methyl alcohol in slender needles, m. p. 142°, and an *anil*, $C_7H_{14}{<}\begin{matrix}CO\\CO\end{matrix}{>}NPh$, separating from benzene in silky needles, m. p. 163°. On reduction with sulphuric acid, 1 : 1-diethyl-Δ^2-*cyclo*pentene gives 1 : 2-diethyl*cyclo*pentane.

2-*Bromo*-1 : 1-*diethyl*cyclo*pentane*, $C_9H_{17}Br$, has b. p. 105—106°/24 mm., D_0^{20} 1·2005, n_D 1·4895, and, on reduction with a copper-zinc couple, gives 1 : 1-*diethyl*cyclo*pentane*, $C_5H_8Et_2$, b. p. 150·5°/757 mm., D_0^{20} 0·8028, n_D 1·4388. T. H. P.

Syntheses in the Fatty Aromatic Series. II. Julius von Braun [with H. Deutsch and O. Kruber] (*Ber.*, 1911, **44**, 2867—2881. Compare Abstr., 1910, i, 843).—At the present time there are, for the conversion of an alcohol into the next higher homologue, three practical methods, represented by the following schemes: (i) $R\cdot OH \longrightarrow RCl \longrightarrow R\cdot CN \longrightarrow R\cdot CO_2H \longrightarrow R\cdot CO_2Et \longrightarrow R\cdot CH_2\cdot OH$, (ii) $R\cdot OH \longrightarrow RBr \longrightarrow R\cdot MgBr \xrightarrow{(CH_2O)_3} R\cdot CH_2\cdot OH$, (iii) $R\cdot OH \longrightarrow RCl \longrightarrow R\cdot CN \longrightarrow R\cdot CH_2\cdot NH_2 \longrightarrow R\cdot CH_2\cdot NHBz \xrightarrow{PCl_5} R\cdot CH_2Cl \longrightarrow R\cdot CH_2\cdot OH$. All these methods are efficacious for the conversion of γ-chloropropylbenzene into δ-phenylbutyl alcohol method (ii) giving the best result. For the synthesis of yet higher alcohols, however, only methods (i) and (iii) are practicable, the latter being the more convenient, since larger quantities can be manipulated at a time. In this way derivatives of phenylheptane have been prepared.

Ethyl γ-phenylbutyrate, $CH_2Ph\cdot CH_2\cdot CH_2\cdot CO_2Et$, b. p. 130—131°/10 mm., is reduced by sodium and alcohol to *δ-phenylbutyl alcohol*, $CH_2Ph\cdot[CH_2]_2\cdot CH_2\cdot OH$, b. p. 140°/14 mm., in 70% yield; the alcohol, which has a strong, unpleasant odour, forms a *phenylurethane*,

$$C_{17}H_{19}O_2N,$$

m. p. 51—52°, and is converted by concentrated hydrobromic acid at 100° into *δ-bromobutylbenzene*, b. p. 131—133°/12 mm. *ε-Phenylamyl alcohol*, $CH_2Ph\cdot[CH_2]_3\cdot CH_2\cdot OH$, b. p. 155°/20 mm., can be prepared in less than 50% yield from this bromide, magnesium, and trioxymethylene, but is obtained quantitatively by converting ε-chloroamylbenzene into *ε-phenylamyl acetate*, $CH_2Ph\cdot[CH_2]_4\cdot OAc$, b. p. 155°/12 mm., by boiling acetic acid and potassium acetate and hydro-

lysing the ester by alcoholic alkali; it has an extremely pleasant, but not very persistent, odour of citron.

ε-Phenylhexonitrile, $CH_2Ph\cdot[CH_2]_4\cdot CN$, b. p. 160—164°/13 mm., prepared from ε-iodoamylbenzene and potassium cyanide in boiling aqueous alcohol, yields by hydrolysis *ε-phenylhexoic acid*, b. p. 180—190°/17 mm. (*ethyl* ester, b. p. 161—163°/13 mm.), and by reduction with sodium and alcohol, *ζ-phenylhexylamine*,

$$CH_2Ph\cdot[CH_2]_5\cdot NH_2,$$

b. p. 144—146°/15 mm., which absorbs moisture and carbon dioxide; it forms a *picrate*, m. p. 99—100°, *benzoyl* derivative, m. p. 59—61°, *platinichloride*, m. p. 216—220° (decomp.), *aurichloride*, m. p. 71—72°, and quaternary *methiodide*, $CH_2Ph\cdot[CH_2]_5\cdot NMe_3I$, m. p. 172°.

ζ-Chlorohexylbenzene, $CH_2Ph\cdot[CH_2]_5\cdot Cl$, b. p. 142—146°/15 mm., prepared by fusing the preceding benzoyl derivative with phosphorus pentachloride, has a pleasant odour less intense than that of ε-chloroamylbenzene, and is converted into the almost odourless *ζ-iodohexylbenzene*, b. p. 168—173°/15 mm., by sodium iodide in the usual manner. *ζ-Phenylhexyl alcohol*, b. p. 160—161°/13 mm., obtained by the reduction of ethyl ε-phenylhexoate, has a not particularly pleasant odour, less intense than that of the phenylamyl alcohol, forms an *acetate*, b. p. 166—168°/13 mm., and is converted by concentrated hydrochloric acid at 120° into the preceding chlorohexylbenzene, and by hydrobromic acid at 125° into *ζ-bromohexylbenzene*, b. p. 160—161°/17 mm.

ζ-Phenylheptonitrile, $CH_2Ph\cdot[CH_2]_5\cdot CN$, b. p. 173—178°/15 mm., obtained from iodohexylbenzene and potassium cyanide, has a very intense, persistent odour, and yields by hydrolysis *ζ-phenylheptoic acid*, b. p. 205—210°/17 mm. (*amide*, m. p. 89°), from the *ethyl* ester, b. p. 175—177°/16 mm., of which is obtained *η-phenylheptyl alcohol*,

$$CH_2Ph\cdot[CH_2]_6\cdot OH,$$

b. p. 170—172°/15 mm. This alcohol has a pleasant odour of roses, which is less intense than that of the phenylhexyl alcohol (attention is particularly called to the alternating intensity of the odour of these homologous alcohols); its *acetate* has b. p. 188—190°/24 mm. *η-Phenylheptylamine*, b. p. 159—160°/16 mm., obtained by the reduction of the preceding nitrile, forms a *picrate*, m. p. 120—122°, *platinichloride*, m. p. 210—213° (decomp.), *aurichloride*, m. p. 103°, and quaternary *methiodide*, $CH_2Ph\cdot[CH_2]_6\cdot NMe_3I$, m. p. 164°. By the distillation of its oily *benzoyl* derivative with phosphorus pentachloride is obtained *η-chloroheptylbenzene*, b. p. 159—164°/17 mm.; the corresponding *bromide* and *iodide* have b. p. 170—175°/15 mm. and 179—184°/17 mm. respectively. The iodide combines with trimethylamine to form the preceding methiodide.

β-Chloroethylbenzene is conveniently obtained by reducing benzyl cyanide with sodium and alcohol, and distilling the benzoyl derivative of the resulting β-phenylethylamine (which need not be isolated) with phosphorus pentachloride; the yield is 65—70%. C. S.

Trinaphthylmethane Compounds. ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1022—1039).—Further investigation of the alcohol described by Schmidlin and Massini (Abstr.,

1909, i, 563) as tri-α-naphthylcarbinol and of the hydrocarbon, regarded as tri-α-naphthylmethane, obtained by the author by reduction of the carbinol (this vol., i, 436), shows that these compounds are really α-naphthyldi-$\alpha\alpha$-naphthafluoryl alcohol (I) and α-naphthyldi-$\alpha\alpha$-naphthafluorene (II) respectively:

$$C_{10}H_7\cdot C(OH)<\begin{matrix}C_{10}H_6\\ |\\ C_{10}H_6\end{matrix} \qquad C_{10}H_7\cdot CH<\begin{matrix}C_{10}H_6\\ |\\ C_{10}H_6\end{matrix}.$$

(I.) (II.)

This stable carbinol, described by Schmidlin and Massini, is found to be formed as a result of the oxidising action of atmospheric oxygen on the unstable tri-α-naphthylcarbinol, with which it has no reactions in common, thus: $C_{31}H_{22}O + O_2 = C_{31}H_{20}O + H_2O_2$. This oxidation may also be carried out by means of neutral permanganate solution. These constitutions of the two compounds and that of the reduction product of the stable carbinol referred to above are confirmed by the previous and also by new analytical results.

Contrary to the opinion of Schmidlin and Massini, the yellow colour of the bromo-derivative (see below) of α-naphthyldi-$\alpha\alpha$-naphthafluoryl alcohol is probably due to its paraquinonoid structure,

$$(C_{10}H_7)_2{:}C{:}C<\begin{matrix}-C_6H_4-\\ CH{:}CH\end{matrix}>CHBr.$$

Also the red colour of the solution of this alcohol in sulphuric acid may be due to the formation of an oxonium compound,

$$(C_{10}H_7)_3{\vdots}C\cdot O\begin{matrix}\diagup H\\ -H\\ \diagdown OSO_3H\end{matrix},$$

and the blue colour obtained on heating this solution to loss of water and formation either of a carbonium salt, $(C_{10}H_7)_3{\vdots}C\cdot OSO_3H$, or, more probably, of a complex compound of the type

$$(C_{10}H_7)_3{\vdots}C\cdot O\cdot SO_3H,(H_2SO_4)_x.$$

Di-α-naphthyl ketone, obtained by the oxidation of di-α-naphthylcarbinol with sulphuric acid and potassium dichromate, forms large, yellow prisms, m. p. 98°. In view of the higher melting point (104°) of the colourless compound obtained by Schmidlin and Massini (Abstr., 1909, i, 561), it is regarded as possible that this ketone exhibits polymorphism.

Tri-α-naphthylcarbinol, $C_{31}H_{22}O$, prepared by the interaction of di-α-naphthyl ketone and magnesium α-naphthyl bromide in presence of ether, forms compounds with both ether and benzene, the former showing the greater inclination to oxidise in the air; both these compounds dissolve with some difficulty in sulphuric acid, giving pale yellow solutions, whilst the stable carbinol dissolves readily and forms an intense red solution. The amount of the solvent in the dry benzene compound cannot be determined by analysis. The carbinol free from solvent forms drusy masses of large, colourless prisms, m. p. 140—160° (decomp.). The hydroxyl group of tri-α-naphthylcarbinol is readily replaceable by halogens; thus the action of hydriodic acid in the cold on an acetic acid solution of the carbinol gives *iodotri-α-naphthylmethane*, $CI(C_{10}H_7)_3$, which crystallises in slender, unstable, white needles, decomposing at 159°; the corresponding *bromo*-derivative forms slender, white needles, m. p. 178° (decomp.).

α-Naphthyldi-$\alpha\alpha$-naphthafluoryl alcohol, obtained by oxidation of tri-α-naphthylcarbinol, crystallises from acetic acid in yellow prisms, m. p. 165°, and does not give the reaction for hydroxyl. α-Naphthyldi-$\alpha\alpha$-naphthafluoryl bromide, $C_{31}H_{19}Br$, forms an intensely lemon-yellow, crystalline powder, decomposing at 215—218°, and gives a deep blue solution with concentrated sulphuric acid. Reduction of the bromide with hydriodic acid yields α-naphthyldi-$\alpha\alpha$-naphthafluorene, m. p. 191°, identical with that obtained by reduction of α-naphthyldi-$\alpha\alpha$-naphthafluoryl alcohol (compare this vol., i, 436). T. H. P.

Preparation of Cholesteryl Ethers. OTTO DIELS and PAUL BLUMBERG (*Ber.*, 1911, **44**, 2847—2851).—The following cholesteryl ethers have been prepared by heating magnesium and cholesteryl chloride with the corresponding alcohol; the numbers in parenthesis denote the temperature and time of heating. *Methyl ether*, $C_{27}H_{45}\cdot OMe$, m. p. 84° (125°, twelve hours); *ethyl ether*, $C_{27}H_{45}\cdot OEt$, m. p. 88—90°, long needles (140°, eighteen hours); *propyl ether*, $C_{27}H_{45}\cdot OPr^{\alpha}$, m. p. 99·5—100·5°, long prisms (140—150°, six hours); benzyl ether, m. p. 114—115° (Obermüller gives 78°) (170°, seven hours).

An attempt to prepare α-cholestyl methyl ether from magnesium, α-cholestyl chloride, and methyl alcohol (140°, eight hours) led to the formation of a *hydrocarbon*, $C_{27}H_{46}$, m. p. 56°, leaflets or prisms.

C. S.

Some Ethers of Cholesterol. WILHELM STEINKOPF and ERWIN BLÜMMER (*J. pr. Chem.*, 1911, [ii], **84**, 460—472).—When heated with ethyl iodide, the potassium derivative of cholesterol yields ethylene and cholesterol; with cholesteryl chloride it forms cholesterol and cholesterylene (compare Lindenmeyer, *J. pr. Chem.*, 1863, [i], **90**, 321).

By heating cholesteryl chloride with zinc dust or zinc oxide, Mauthner and Suida (Abstr., 1896, i, 425) obtained a substance which they considered to be cholesteryl ether. The authors have repeated these experiments, and find that the product consists of cholesterylene together with a small quantity of a substance, m. p. 210—225°.

Cholesteryl phenyl ether, $C_{27}H_{45}\cdot OPh$, obtained by heating cholesteryl chloride with sodium phenoxide, crystallises in lustrous, silvery leaflets, m. p. 157·5°, and has, in chloroform solution, $[\alpha]_D - 34·89°$; the p-*tolyl ether*, prepared in a similar manner, has m. p. 154·5°, $[\alpha]_D - 32·95°$ in chloroform solution. The benzyl ether, obtained by heating the potassium derivative of cholesterol with benzyl chloride at 100°, forms small, white needles, m. p. 118·5°, $[\alpha]_D - 26·02°$ (compare preceding abstract).

Cholesteryl p-*methylbenzyl ether*, $C_{27}H_{45}\cdot O\cdot CH_2\cdot C_6H_4Me$, prepared from ω-bromo-p-xylene in a similar manner, exists in several solid and liquid crystalline modifications. It melts at 129—130° to a a turbid, opalescent liquid, which becomes clear at 141·5°; on cooling, the liquid again becomes turbid, and acquires a deep violet colour, which then passes successively into blue, green, red, and pink, solidification finally taking place at 130°; in chloroform solution it has $[\alpha]_D - 26·32°$. The m-*methylbenzyl ether* melts at 93—94° to a turbid

liquid, which becomes isotropic at 125°, and shows the same colour changes as the preceding compound; in chloroform solution it has $[\alpha]_D$ −31·76°. A microcrystallographic examination of the two last-mentioned ethers is given by Lehmann. F. B.

l-Phytosterols. II. Timothée Klobb (*Ann. Chim. Phys.*, 1911, [viii], 24, 410—421. Compare Abstr., 1910, i, 31; ii, 1100; 1911, i, 199).—The phytosterols of *Matricaria chamomilla, Tilia europea, Linaria vulgaris,* and *Verbascum thapsus* are described.

The oily matter left after the deposition of hydrocarbon by the acetone extract of *Matricaria chamomilla* (Abstr., 1910, ii, 1100) on treatment with potassium hydroxide in alcohol yields to ether a small amount of unsaponifiable matter, which after solution in hot alcohol deposits a mixture (m. p. 120—131°, α_D −29·3°) of needles and hexagonal lamellæ. This mixture gives the colour reactions of the l-phytosterols, and in addition a purple coloration with sulphuric acid containing nitrous acid. Acetic anhydride converts it into a mixture of acetyl derivatives, m. p. 150—175°, crystallising in lamellæ and flattened prisms. The mixture on bromination separates into a *substance*, $C_{36}H_{68}OAc,Br_4$, m. p. 158—160°, crystallising in hexagonal lamellæ, and a *product*, $C_{36}H_{43}OAc,Br_2$, m. p. 115—118°, which crystallises from benzene, on addition of alcohol, in microscopic granules.

[With J. Garnier, in part.]—The unsaponifiable matter from the flowers of *Tilia europea* contains a phytosterol, $C_{27}H_{46}O$, α_D −29·7°, m. p. 126°, crystallising in hexagonal lamellæ, and giving normal colour reactions; the *benzoyl* derivative, m. p. 140°, and the *acetyl* derivative, m. p. 118—119°, crystallise in hexagonal lamellæ. The second of these gives a *dibromo*-compound, $C_{26}H_{43}OAc,Br_2$, m. p. 115—120°, which separates from benzene on addition of alcohol in microscopic granules.

The phytosterol, $C_{26}H_{44}O$, obtained from *Linaria vulgaris* (Abstr., 1907, ii, 123), gives a *benzoyl* derivative, α_D − 14·55°, m. p. 142°, crystallising in nacreous, rectangular lamellæ, and an *acetyl* derivative, α_D −38·61°, m. p. 117—130°, which crystallises simultaneously in hexagonal lamellæ and short prisms, and may be a mixture.

[With R. Ehrwein.]—The flowers of *Verbascum thapsus* treated by the general process (Abstr., 1910, ii, 1100) furnish *verbasterol*, α_D −3°3′, m. p. 142—144°, containing carbon 82·05% and hydrogen 11·89%, and crystallising in pearly, hexagonal lamellæ. On treatment with acetic anhydride two *substances* are formed; the *one* has m. p. 169—171°, and the *other*, m. p. 108—110°. It is impossible at present to say whether in this and the previous case the two acetyl derivatives are isomerides derived from the same phytosterol, or whether the original substance is a mixture and is resolved into its components by acetylation. T. A. H.

3:4-Dihydroxybenzyl-methyl and -dimethyl Amines. Marc Tiffeneau (*Bull. Soc. chim.*, 1911, [iv], 9, 928—932).—These two bases, which are closely related to adrenaline and exhibit a similar but far weaker physiological action, are described.

3 : 4-*Dimethoxybenzyl alcohol* (*veratryl alcohol*), D^{16} 1·180, b. p. 169°/14 mm., obtained by the action of potassium hydroxide on veratraldehyde, is a viscous liquid ; the *acetate*, b. p. 170—175°/13 mm., is a thick liquid ; the *benzoate*, D^0 1·203, m. p. 36—37°, b. p. 233—236°/12 mm., crystallises on long keeping ; the *phenylurethane*, m. p. 118°, is crystalline.

3 : 4-*Dimethoxybenzyl chloride*, m. p. 48°, is crystalline, and when heated with methylamine in a closed tube furnishes 3 : 4-*dimethoxybenzylmethylamine*, b. p. 135—140°/12 mm., the *hydriodide* of which has m. p. 170—171°. On demethylation, the base yields 3 : 4-*dihydroxybenzylmethylamine*, m. p. 179°, the *hydrochloride* of which has m. p. 182°.

When heated with dimethylamine in a closed tube, or when treated with this substance in dilute ethereal solution, 3 : 4-dimethoxybenzyl chloride yields 3 : 4-*dimethoxybenzyldimethylamine*, D^0 1·0578, b. p. 132—137°/12 mm., or 236—239°/760 mm., as a colourless liquid. This gives a *hydriodide*, m. p. 174°, a *methiodide*, m. p. 179°, and with acid anhydrides or chlorides furnishes the corresponding acyldimethylamines and dimethoxybenzyl esters. On demethylation of the parent base, 3 : 4-*dihydroxybenzyldimethylamine* is obtained, yielding a *hydrochloride*, m. p. 183°, which may also be prepared by the action of phosphorus pentachloride on 3 : 4-*methylenedioxybenzyldimethylamine*, D^0 1·101, b. p. 125°/13 mm. The latter was obtained by heating piperonyl chloride (Decker and Koch, Abstr., 1905, i, 473) with dimethylamine in a closed tube. The *hydrochloride* has m. p. 223°, the *hydriodide*, m. p. 135°, and the *methiodide*, m. p. 233°.

Piperonyl alcohol furnishes an *acetate*, m. p. 48°, and a phenylurethane, m. p. 102·5°. T. A. H.

2 : 3- and 3 : 4-Dihydroxybenzylamines. René Douetteau (*Bull. Soc. chim.*, 1911, [iv], 9, 932—938. Compare preceding abstract).—These substances were prepared with a view to comparing their physiological action with that of adrenaline.

2 : 3-*Dimethoxybenzylamine*, D^0 1·1243, b. p. 137°/11 mm., obtained by reduction of 2 : 3-dimethoxybenzaldoxime (Noelting, Abstr., 1910, i, 176), is a colourless, oily liquid ; the *hydrochloride*, m. p. 159°, is crystalline ; the *picrate*, m. p. 205°, forms golden-yellow needles ; the *methiodide* has m. p. 174° ; the *acetyl* derivative, m. p. 94°, b. p. 210—211°/10 mm., is crystalline, and when treated with sodium in boiling benzene and then submitted to the action of methyl iodide furnishes 2 : 3-*dimethoxyphenylacetomethylamide*,

$$C_6H_3(OMe)_2\cdot CH_2\cdot NMeAc,$$

D^0 1·1506, b. p. 202—205°/13 mm. (approx.), as a pale yellow, viscous liquid. When heated with acetic anhydride at 150—160° this decomposes, furnishing the initial amide (compare Tiffeneau, this vol., i, 778).

2 : 3-*Dihydroxybenzylamine hydriodide*, m. p. 149°, obtained by the action of hydriodic acid on the dimethyl ether referred to above, is crystalline, and on treatment with silver chloride yields the *hydrochloride*, m. p. 186° ; both salts give a green coloration with ferric chloride.

3 : 4-*Dimethoxybenzylamine*, b. p. 154—158°/12 mm. (approx.), prepared like its isomeride, is a colourless oil; the *hydrochloride*, m. p. 257°, the *picrate*, m. p. 169°, and the *methiodide*, m. p. 228°, were obtained crystalline. On demethylation by hydriodic acid, 3 : 4-*dihydroxybenzylamine hydriodide*, m. p. 205°, is produced, from which the *hydrochloride*, m. p. 172°, is obtained by agitation with silver chloride. T. A. H.

1-Amino*cyclo*pentane-1-carboxylic Acid. NICOLAI D. ZELINSKY and G. STADNIKOFF (*Zeitsch. physiol. Chem.*, 1911, **75**, 350—351. Compare Abstr., 1906, i, 425).—1-Amino*cyclo*pentane-1-carboxylic acid has been obtained by the interaction of *cyclo*pentanone, ammonium chloride, and potassium cyanide in aqueous alcoholic solution, and subsequent hydrolysis of the nitrile so formed by means of hydrochloric acid. It separates from water in monoclinic crystals containing $1H_2O$, decomp. 320°. The *copper* salt was analysed. H. W.

Naphthenic Acids. I. PETROFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1198—1201).—Crude naphthenic acid from Baku naphtha was carefully purified from neutral substances and then converted into methyl esters, of which the three following were isolated: (1) b. p. 161—163°/748 mm.; the acid from this has b. p. 211—213°, which corresponds with that of Markownikoff's heptanaphthenic acid (Abstr., 1893, i, 93); (2) b. p. 169—171°/748 mm., the acid from which has b. p. 218—220°, corresponding with that of Colman and Perkin's 1-methylpentamethylene-2-carboxylate (Trans., 1888, **53**, 185), and (3) $C_7H_{13}\cdot CO_2Me$, b. p. 177—178°/736 mm., D_0^0 0·9455, $D_{21\cdot 7}^{21\cdot 7}$ 0·9295, $n_D^{21\cdot 7}$ 1·43005.

Reduction of ester (3) by Bouveault and Blanc's method (Abstr., 1903, i, 597) yields the *alcohol*, $C_8H_{15}\cdot OH$, as a colourless, viscous liquid with a pleasant odour, b. p. 183—184°/756 mm., or 103—104°/35 mm., D_0^0 0·8943, $D_{23\cdot 5}^{23\cdot 5}$ 0·8808, $n_D^{23\cdot 5}$ 1·44541.

The alcohol was converted through the xanthate into the naphthylene, b. p. about 108°, which contained an admixture of toluene, and hence was not analysed.

When the ester (3) was heated in a sealed tube with concentrated ammonia solution at 150°, it was converted into a mixture of two amides, which after several fractional crystallisations showed m. p. 117° and 160° respectively, but it is possible that the separation was not complete; it is probable that these two amides are *cis*- and *trans*-isomerides. Two other fractions, b. p. 192° and 200°, were also separated, and are being investigated. T. H. P.

***o*-Amino-*p*-sulphobenzoic Acid and its Derivatives, with Special Reference to their Fluorescence. II.** JOSEPH H. KASTLE and R. L. HADEN (*Amer. Chem. J.*, 1911, **46**, 508—518).—It has been shown in an earlier paper (this vol., i, 200) that when disilver *o*-amino-*p*-sulphobenzoate is treated with ethyl iodide, *o*-ethylamino-*p*-sulphobenzoic acid is produced. In one experiment, a small quantity of a sulphur-yellow compound was obtained, which has now been found to be diethyl *o*-ethylamino-*p*-sulphobenzoate,

$$CO_2Et\cdot C_6H_3(NHEt)\cdot SO_3Et,$$

m. p. 151—153° (uncorr.); it crystallises in yellow needles, and on hydrolysis is converted into *o*-ethylamino-*p*-sulphobenzoic acid.

When *o*-amino-*p*-sulphobenzoic acid (1 mol.) is heated with its disilver salt (1 mol.), an acid silver salt,

$$CO_2H\cdot C_6H_3(NH_2)\cdot SO_3H, CO_2Ag\cdot C_6H_3(NH_2)\cdot SO_3Ag, 2H_2O,$$

is formed, which on being treated with ethyl iodide is converted into a mixture of diethyl *o*-ethylamino-*p*-sulphobenzoate and the original amino-acid.

Comparison has been made of the fluorescence in various solvents of *o*-amino-*p*-sulphobenzoic acid, *o*-ethylamino-*p*-sulphobenzoic acid, and the diethyl ester of the latter. The substitution of an ethyl group for a hydrogen atom of the carboxyl or amino-group has the effect of increasing the blue tint of the fluorescence; thus, in a mixture of equal volumes of water and alcohol, *o*-amino-*p*-sulphobenzoic acid shows a pinkish-purple fluorescence, and the ethylamino-acid a pure blue, whilst the diethyl ester of the latter gives a yellow solution with a pure blue fluorescence.

o-Aminoterephthalic acid exhibits a reddish-blue fluorescence in dilute aqueous and alkaline solutions, and a pure blue fluorescence in acetone solutions. Aqueous solutions of the mono- and di-ethyl esters show a pure blue fluorescence. E. G.

Isomerism of the Three *allo*-Cinnamic Acids. JULIUS MEYER (*Ber.*, 1911, 44, 2966—2970).—Evidence is adduced in support of Biilmann's (Abstr., 1909, i, 155, 382; 1910, i, 346) view of the relationship of the three acids as opposed to Stobbe's explanation of their isomerism (this vol., i, 859).

Biilmann's observation that any one of the three acids may be obtained by inoculating the melted substance with the required acid is confirmed (Abstr., 1909, i, 155) and extended by the observation that a supersaturated solution behaves similarly. A spontaneously crystallised fusion of one form can be converted into a second form by inoculation, and the rate of this transformation descends in the following order, $42° \rightarrow 68° > 42° \rightarrow 58° > 58° \rightarrow 68°$. The velocity of crystallisation is greatest for the 68° acid and least for the 42° acid. The heat developed in the change of one form into either of the other two is too small to be measured. The spontaneously crystallised fusion may consist of all three acids, and no difference in behaviour could be observed whichever form was melted in the first instance. Solutions of all three acids at the same concentration and temperature have the same electrical conductivity (compare Biilmann, Abstr., 1910, i, 346), but the solubility in water is least for the 68° acid and greatest for the 42° acid. All these observations are in harmony with Biilmann's view that the *allo*-cinnamic acids are polymorphous modifications of *cis*-cinnamic acid. T. A. H.

Transformations of *cis*-Cinnamic Acid. HUGO R. KRUYT (*Ber.*, 1911, 44, 3108—3115. Compare Stobbe, this vol., i, 859). To explain Stobbe's results (*loc. cit.*), Tammann's theory of the mechanism of spontaneous crystallisation must be extended to the equilibrium solid–solid. The maximum rate of crystallisation occurs at a much higher temperature than that of the formation of crystalline nuclei. When a

liquid is undercooled and warmed again slightly, no crystallisation takes place at the lower temperature, but it sets in rapidly on warming, owing to the marked formation of nuclei at the lower temperature. Stobbe's results are criticised in detail, and shown to be fully in agreement with this hypothesis. E. F. A.

Compounds of 3:5-Dinitro-4-hydroxybenzoic Acid with Hydrocarbons. II. OTTO MORGENSTERN (*Monatsh.*, 1911, 32, 711—746. Compare Abstr., 1910, i, 482).—It is sought by physical chemical measurements to establish the composition of the coloured compounds of 3 : 5-dinitro-4-hydroxybenzoic acid with aromatic hydrocarbons previously described (Abstr., 1910, i, 482). Measurements have been made of the equilibrium between hydrocarbon and acid in alcoholic solution.

If two molecules of acid combine with one of hydrocarbon $(c_1^2.c_2)/c_3$ = a constant, c_1, c_2, and c_3 being the concentrations of free acid, free hydrocarbon, and of the compound of the two respectively.

The values of c_1, c_2, and c_3 were determined experimentally in two ways. In the first a small proportion of hydrocarbon was added to the saturated solution of acid; in the second a little acid was added to the saturated hydrocarbon solution. The results show that in the second series the expression $(c_1^2.c_2)/c_3$ was not a constant, but that equilibrium was obtained between an equal number of molecules of acid and hydrocarbon, or, in other words, $(c_1.c_2)/c_3$ = a constant. The first series in which acid was in excess pointed to the formation of a compound 2 acid + hydrocarbon as assumed.

Two series of compounds are thus proved to exist in the case of phenanthrene, retene, and fluorene with dinitrohydroxybenzoic acid.

The *compound* acid + phenanthrene crystallises in yellow needles, m. p. 180° (decomp.).

The *compound* acid + fluorene is a yellowish-white powder, m. p. 210—214° (decomp.).

The analogous retene *compound* forms yellow plates, m. p. 220° (decomp.). E. F. A.

Studies on Tautomerism. V. Enolic Forms of Methyl Benzoylacetate and Acetylacetone. LUDWIG KNORR (*Ber.*, 1911, 44, 2767—2772. Compare Meyer, this vol., i, 833).—The enolic forms of methyl benzoylacetate and acetylacetone can be isolated by the methods previously given in the case of ethyl acetoacetate (this vol., i, 516), with the difference that in these cases the enolic and not the ketonic forms crystallise out on strongly cooling solutions of the equilibrium mixtures. Methyl benzoylacetate when dissolved in a mixture of ether and light petroleum deposits at −78° acicular crystals, which can be collected, washed, and dried in the apparatus previously described. The freshly prepared substance has m. p. about 40° (bath previously heated), and gives an intense coloration with alcoholic ferric chloride solution. It has $n_D^{12.5}$ 1·5620, whilst the equilibrium mixture has $n_D^{12.5}$ 1·5418. These properties indicate that it is the enolic form of the ester, and, in fact, the same substance is obtained (but it is not

so pure) by treating an aqueous solution of the pure sodium salt (see below) with the calculated quantity of normal sulphuric acid at 0°. The production of the ketonic form takes place fairly rapidly. The crystals liquefy gradually even in a desiccator, and the oil attains to the refractive index of the equilibrium mixture in the course of hours or days according to the name of the containing vessel.

The sodium and iron salts of the enolic ester were also prepared. The *sodium* salt, $C_{10}H_9O_3Na$, is obtained in small laminæ by mixing at 0° a methyl-alcoholic solution of sodium methoxide with the equivalent quantity of the ester dissolved in ether. The *sodium* salt of ethyl benzoylacetate, $C_{11}H_{11}O_3Na$, is similarly prepared. The *ferric* salt of methyl benzoylacetate, $Fe(C_{10}H_9O_3)_3$, is prepared by mixing at 0° a methyl-alcoholic solution of the ester with an ethereal solution of ferric chloride, and the salt is washed with water until the chlorine reaction disappears. After recrystallisation, it forms red needles, m. p. 188° (previously sintering). From the reaction in dilute ethereal solution of molecular quantities of ferric chloride and the ester, an *iron* salt containing chlorine is obtained. It forms compact, yellow, hygroscopic crystals, which on analysis yield numbers corresponding fairly well with the formula $FeCl_2(C_{10}H_9O_3),3H_2O$. It dissolves in water and alcohol, with production of the deep reddish-violet coloration characteristic of the iron reaction.

[With HERMANN FISCHER.]—The enolic form of acetylacetone has been isolated by strongly cooling solutions of the equilibrium mixture. The crystalline substance has m. p. −9°, n_D^{15} 1·4609. At the ordinary temperature the substance rapidly changes into the allelotropic mixture of diketone and enol-ketone (n_D^{15} 1·4550); at 15° the transformation is complete in twenty minutes By withdrawal of the enolic isomeride with copper hydroxide, preparations containing much of the ketonic form have also been obtained. R. V. S.

General Additive Reaction between Alkylidene-urethanes and β-Dicarboxylic Compounds. G. BIANCHI and ROBERT SCHIFF (*Gazzetta*, 1911, **41**, ii, 81—93).—When a concentrated alcoholic solution of equimolecular quantities of ethyl acetoacetate and urethane are treated with a corresponding quantity of benzaldehyde and a few drops of concentrated hydrochloric acid, the mixture becomes solid in a few minutes (formation of benzylidenediurethane), then liquefies, and finally solidifies two days later. The substance produced (compare Schiff and Bertini, Abstr., 1897, i, 493) is the additive product, *ethyl urethanobenzylacetoacetate*, $CO_2Et\cdot CHAc\cdot CHPh\cdot NH\cdot CO_2Et$, which is a white, microcrystalline powder, m. p. 96—97°. When slightly warmed with concentrated sulphuric acid, it gives a red coloration. The analogous compounds described were similarly prepared, and the reaction appears to be a general one.

Ethyl urethanobenzylbenzoylacetate,

$$CO_2Et\cdot CHBz\cdot CHPh\cdot NH\cdot CO_2Et,$$

is a white, minutely crystalline powder, m. p. 97°.

Urethanobenzylacetylacetone, $CHAc_2\cdot CHPh\cdot NH\cdot CO_2Et$, forms a white, crystalline powder, m. p. 101°; its alcoholic solution gives a red coloration with ferric chloride when warmed.

Ethyl urethanocinnamylacetoacetate,

$CHPh{:}CH\cdot CH(NH\cdot CO_2Et)\cdot CHAc\cdot CO_2Et$,

is a white, microcrystalline powder, m. p. 92—93°.

Urethanocinnamylacetylacetone, $CHPh{:}CH\cdot CH(CHAc_2)\cdot NH\cdot CO_2Et$, is a white, microcrystalline powder, m. p. 107°, and gives an intense red coloration with ferric chloride.

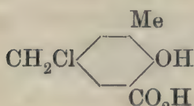
Urethanoanisylacetylacetone, $OMe\cdot C_6H_4\cdot CH(CHAc_2)\cdot NH\cdot CO_2Et$, is a white, crystalline powder, m. p. 98°; with ferric chloride it gives an intense red coloration.

Urethanosalicylacetylacetone, $OH\cdot C_6H_4\cdot CH(CHAc_2)\cdot NH\cdot CO_2Et$, is a white, crystalline powder, m. p. 128—130°, and gives a red coloration with ferric chloride.

All the compounds described are very stable towards mineral acids. R. V. S.

Preparation of Unsymmetrical Substituted Diphenylmethane Derivatives. ANILINFARBEN- & EXTRAKT-FABRIKEN VORM. JOH. RUD. GEIGY (D.R.-P. 236046).—When 2-hydroxy-*m*-toluic acid is treated with chloromethyl alcohol (or analogous reagents) in the presence of fuming hydrogen chloride, condensation takes place in the para-position to the hydroxyl group.

2-*Hydroxy*-3-*methyl*-5-*chloromethylbenzoic acid* (annexed formula) is a colourless, crystalline powder, m. p. 197°; when heated with water it furnishes, in part, 2-*hydroxy*-3-*methyl*-5-*hydroxymethylbenzoic acid*, $CO_2H\cdot C_6H_2Me(OH)\cdot CH_2\cdot OH$, hard prisms, m. p. 186°; in part, the *anhydro-compound* an amorphous, colourless, insoluble, infusible powder.



2-*Hydroxy*-5-*diethylaminobenzyl*-3-*methylbenzoic acid* is prepared by heating 2-hydroxy-3-methyl-5-chloromethylbenzoic acid with diethylaniline, first at 70°, and subsequently at 100°; the *sodium* salt forms glistening leaflets, and the free acid crystallises in tablets, m. p. 171°.

2-*Hydroxy*-5-*ethylaminotolylmethyl*-3-*methylbenzoic acid*, glistening prisms, m. p. 184°, is prepared from 2-hydroxy-3-methyl-5-hydroxymethylbenzoic acid (or its anhydro-compound) and ethyl-*o*-toluidine in the presence of hydrogen chloride at 110—120°; the *sodium* salt forms glistening leaflets.

2-*Hydroxy*-5-*methylaminobenzyl*-3-*methylbenzoic acid*, leaflets, m. p. 193°; 2-*hydroxy*-5-*dimethylaminobenzyl*-3-*methylbenzoic acid*, glistening, silvery scales, m. p. 195°; 2-*hydroxy*-5-*dimethylaminotolylmethyl*-3-*methylbenzoic acid*, glistening, pearly leaflets, m. p. 167°; 2-*hydroxy*-5-*diethylaminochlorobenzyl*-3-*methylbenzoic acid*, prisms, m. p. 152°, and 2-*hydroxy*-5-*diethylaminodichlorobenzyl*-3-*methylbenzoic acid*, needles, m. p. 230°, were also prepared. F. M. G. M.

Action of Sodium Amalgam on Naphtholcarboxylic Acids. HUGO WEIL (*Ber.*, 1911, 44, 3058—3062).—When reduced with sodium amalgam in aqueous solution in the presence of boric acid and

sodium hydrogen sulphite, α-naphthol-2-carboxylic acid yields 1-hydroxy-2-naphthaldehyde (Bezdzik and Friedländer, Abstr., 1909, i, 416).

β-Naphthol-3-carboxylic acid is reduced, under similar conditions, to tetrahydronaphthaldehyde, and β-naphthoic acid to β-naphthaldehyde, whilst α-naphthoic acid remains unchanged.

[With Walter Heerdt.]—4-Sulphoxyl-α-naphthol-2-carboxylic acid is converted into 1-hydroxy-2-naphthaldehyde, the sulphoxyl group being eliminated during the reduction.

4-Bromo-α-naphthol-2-carboxylic acid, obtained by brominating α-naphthol-2-carboxylic acid in glacial acetic acid solution (compare Schmitt and Burkhard, Abstr., 1888, 59), is reduced by sodium amalgam to 4-*bromo*-1-*hydroxy*-2-*naphthaldehyde*. This crystallises in yellow needles, m. p. 112°, yields a *phenylhydrazone*, m. p. 159°, and condenses with primary aromatic amines, yielding anils; the *compound*, $C_{17}H_{12}ONBr$, obtained from aniline, forms orange-yellow needles, m. p. 161°; the *compounds*, $C_{18}H_{14}ONBr$, formed by condensation with *o*- and *p*-toluidine crystallise in yellowish-red needles, m. p. 188° and 171° respectively; the *compound* from α-naphthylamine has m. p. 196°.

4-*Chloro*-α-*naphthol*-2-*carboxylic acid*, $C_{11}H_7O_3Cl$, prepared by chlorinating α-naphthol-2-carboxylic acid in glacial acetic acid solution, has m. p. 228°. It is reduced by sodium amalgam to 4-*chloro*-1-*hydroxy*-2-*naphthaldehyde*, which crystallises in yellow needles, m. p. 103°, and yields an *oxime*, m. p. 194°, and a *phenylhydrazone*, m. p. 153°; the *azine*, $C_{22}H_{14}O_2N_2Cl_2$, forms yellow needles, m. p. 179°. The aldehyde yields a *sodium* salt, crystallising in yellow leaflets, and condenses with aniline, yielding the *anil*, $C_{17}H_{12}ONCl$, which crystallises in yellow needles, m. p. 157°; with α-naphthylamine it forms the *compound*, $C_{21}H_{14}ONCl$, reddish-yellow leaflets, m. p. 188°; the *compounds*, $C_{18}H_{14}ONCl$, obtained by condensation with *o*- and *p*-toluidine are orange-yellow, and have m. p. 183° and 164° respectively. F. B.

Addition of Hydrogen Bromide to Cinnamylidenemalonic Acid, Cinnamylideneacetic Acid, and Phenylbutadiene. C. N. Riiber (*Ber.*, 1911, 44, 2974—2978).—The addition of hydrogen bromide (1 mol.) to methyl cinnamylidenemalonate (compare Hinrichsen, Abstr., 1904, i, 1012) and to methyl cinnamylideneacetate in the $\alpha\beta$-position (contrary to the predictions of Thiele's theory) has been proved as follows. Ethereal solutions of the respective esters are treated with hydrogen bromide; the solution of the additive compound is treated with magnesium and subsequently with water, the resulting product being finally oxidised by potassium permanganate. In both cases benzoic and succinic acids are obtained. The reaction between α-phenyl-$\Delta^{\alpha\gamma}$-butadiene and ethereal hydrogen bromide yields, in addition to a small quantity of a crystalline *substance*, $C_{10}H_9Br,2HBr$, m. p. 146°, an unstable *oil*, CHPh:CH·CHBrMe, which reacts with ethereal zinc methyl at 100° to form a *hydrocarbon*, $C_{11}H_{14}$, b. p. 84—86°/13 mm., from which benzoic and *iso*butyric acids are obtained by oxidation with potassium permanganate. C. S.

[Preparation of Derivatives of Anthraquinonecarboxylic Acids and of Anthraquinoneacridones.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 237236 and 237237).—Condensation products of chloro- and amino-anthraquinones have previously been described; it is now found that similar condensations take place with halogen- or nitro-anthraquinonecarboxylic acids (or bases) in the presence of condensing agents, such as aluminium chloride, sulphuric acid, or copper.

1-*Anilinoanthraquinone*-2-*carboxylic acid* is prepared by heating 1-nitro- or 1-chloro-anthraquinone-2-carboxylic acid with aniline at 120—130° in the presence of copper powder and anhydrous sodium acetate; it forms glistening, brown leaflets, m. p. 297—298°; the *sodium* salt, glistening, violet-black needles, gives a deep violet solution in water, and when heated at 50—60° with phosphorus pentachloride in benzene solution with aluminium chloride furnishes an *anthraquinoneacridone* as a violet-red powder.

p-*Toluidino*-1-*anthraquinone*-2-*carboxylic acid*, a violet powder, is similarly obtained with *p*-toluidine.

4′-*Chloro*-1-*anilinoanthraquinone*-2-*carboxylic acid*, a carmine-red powder, is furnished by the employment of *p*-chloroaniline.

1-*Naphthylamino*-1-*anthraquinone*-2-*carboxylic acid* is a violet powder, and the *product* from 1-chloroanthraquinone-2-carboxylic acid (2 mols.) and 4 : 4′-diaminodiphenylmethane (1 mol.), a violet-red powder, all of which furnish the corresponding *anthraquinoneacridone* on treatment with phosphorus pentachloride.

The colours of the solutions given by these substances in various solvents and other tinctorial properties are described in the original.

The second patent describes the preparation of 1-*anilinoanthraquinone*-2-*carboxyl chloride*, glistening, reddish-brown leaflets, by the action of phosphorus pentachloride on a benzene solution of the foregoing acid at 50—60°; this, by heating at 200° with trichlorobenzene until the evolution of hydrogen chloride ceases, yields the anthraquinoneacridone in violet-red needles.

1-*Naphthylaminoanthraquinone*-2-*carboxyl chloride*, a reddish-brown powder, is obtained by treating the corresponding acid with thionyl chloride, and on boiling with xylene furnishes the anthraquinoneacridone. F. M. G. M.

Oxidation of Phthalacene. D. MAROTTA (*Gazzetta*, 1911, 41, ii, 59—63).—The oxidation of the methyl group of phthalacene (compare Errera, Abstr., 1908, i, 183) can be effected by means of nitric acid, and 3 : 4 : 5 : 6-dibenzoylenebenzoic acid, $\begin{array}{l} C_6H_4\cdot C\text{————————}C\cdot CO \\ CO\text{—}C\cdot C(CO_2H){:}CH\cdot C\cdot C_6H_4 \end{array}$, is produced. From this, on reduction, 3 : 4 : 5 : 6-dibenzylenebenzoic acid, $\begin{array}{l} C_6H_4\cdot C\text{————————}C\cdot CH_2 \\ CH_2\text{—}C\cdot C(CO_2H){:}CH\cdot C\cdot C_6H_4 \end{array}$, is obtained. 3 : 4 : 5 : 6-*Dibenzoylenebenzoic acid* is prepared by heating phthalacene with dilute nitric acid (D 1·035) in a sealed tube for five hours at 200°. In this way nitration is avoided, but the reaction must be completed by opening the tube, decanting the liquid, adding more acid, and then re-heating

at 200° for five hours. The substance is an orange-red powder, m. p. 299—300°. The *potassium* salt, $C_{21}H_9O_4K,3H_2O$, can be prepared, but is very readily hydrolysable. From it the *silver* salt is obtained, and from this the *ethyl* ester, $C_{20}H_9O_2{\cdot}CO_2Et$, which forms silky, yellow needles, m. p. 230°.

3 : 4 : 5 : 6-*Dibenzylenebenzoic acid* is obtained by heating the above acid with hydriodic acid and phosphorus in a sealed tube for five hours at 200°; it forms minute, pale yellow needles, m. p. above 300°. The alkali salts can be hardly isolated on account of their hydrolysability. From the *silver* salt the *ethyl* ester (brown crystals, m. p. 136—137°) was prepared. R. V. S.

Derivatives of Phthalic Acid Containing Sulphur and Nitrogen. ARNOLD REISSERT and HERMANN HOLLE (*Ber.*, 1911, 44, 3027—3040).—Thiophthalic anhydride, $C_6H_4<^{CO}_{CO}>S$, m. p. 114°, is conveniently prepared by triturating phthalic anhydride and crystallised sodium sulphide in a mortar, adding water, and pouring the mixture into dilute hydrochloric acid; the product is freed from phthalic acid by repeated extraction with aqueous sodium carbonate. It is converted into phthalide by reduction with 8% sodium amalgam.

Ethyl thiolphthalate, $CO_2Et{\cdot}C_6H_4{\cdot}CO{\cdot}SEt$, b. p. about 194°/10 mm., is obtained by treating thiophthalic anhydride with cold alcoholic sodium ethoxide, and adding ethyl iodide. In a similar manner the isomeric esters, $CO_2R{\cdot}C_6H_4{\cdot}CO{\cdot}SR'$ and $CO_2R'{\cdot}C_6H_4{\cdot}CO{\cdot}SR$, have been prepared; thus (S)-*methyl ethyl thiolphthalate*,

$$CO_2Et{\cdot}C_6H_4{\cdot}CO{\cdot}SMe,$$

b. p. 209°/16 mm., D 1·1923, is obtained by adding methyl iodide to thiophthalic anhydride in alcoholic sodium ethoxide, and yields phthalic acid, ethyl alcohol, and methyl mercaptan by hydrolysis, whilst *methyl* (S)-*ethyl thiolphthalate*, $CO_2Me{\cdot}C_6H_4{\cdot}CO{\cdot}SEt$, b. p. 209°/16 mm., D 1·1906, is prepared by adding ethyl iodide to the anhydride in methyl-alcoholic sodium methoxide, and yields phthalic acid, methyl alcohol, and ethyl mercaptan by hydrolysis. When chloro-2 : 4-dinitrobenzene in methyl alcohol is added to a cold methyl-alcoholic solution of sodium methoxide and thiophthalic anhydride, and the mixture is subsequently boiled, tetranitrodiphenyl sulphide and (S)-2 : 4-*dinitrophenyl methyl thiolphthalate*, $CO_2Me{\cdot}C_6H_4{\cdot}CO{\cdot}S{\cdot}C_6H_3(NO_2)_2$, m. p. 121°, yellow prisms, are obtained. *Methyl dithiolphthalate*, $C_6H_4(CO{\cdot}SMe)_2$, m. p. 124°, yellowish-brown leaflets or needles, is obtained by the addition of methyl sulphate to the liquid produced by the trituration of thiophthalic anhydride and crystallised sodium sulphide.

Thiophthalanil, $C_6H_4<^{CO}_{CS}>NPh$, m. p. about 144°, long, red needles, is obtained in 80% yield by heating phthalanil and phosphorus pentasulphide in boiling xylene containing a little aniline as a sulphur-carrier, and is purified best by conversion into thiophthalanilic acid by alcoholic sodium hydroxide, the acid being reconverted into the anhydride by boiling with water. The hydrolysis of thiophthalanil by *N*-sodium hydroxide and alcohol, and the subsequent oxidation of the product by potassium ferricyanide, yields *benzthiazole*-1-o-*benzoic acid*,

$CO_2H\cdot C_6H_4\cdot C{<}{}^{S}_{N}{>}C_6H_4$, m. p. 189°, the *methyl* ester of which has m. p. 73°; the *hydrochloride*, $C_{14}H_9O_2NS,HCl$, and the *copper* and *calcium* salts are described, the latter yielding 1-phenylbenzthiazole by distillation.

Iminophthalanil, $C_6H_4{<}{}^{CO\text{———}}_{C(:NH)}{>}NPh$, m. p. 170°, yellow needles, obtained from thiophthalanil and carbamide at 140—150°, dissolves in alkalis and in dilute acids, and yields *methyliminophthalanil*, $C_6H_4{<}{}^{CO\text{———}}_{C(:NMe)}{>}NPh$, m. p. 145°, with methyl sulphate in alkaline solutions, and *benzyliminophthalanil*, m. p. 120°, with benzyl chloride and alcoholic sodium ethoxide. *Oximinophthalanil*,

$$C_6H_4{<}{}^{CO\text{———}}_{C(:NOH)}{>}NPh,$$

m. p. 246° (decomp.), prepared from thiophthalanil, hydroxylamine sulphate, and sodium carbonate in alcoholic solution, is very stable, and has a strongly acidic, but no basic, character. The bromination of iminophthalanil in chloroform yields *bromoiminophthalbromoanil dibromide*, $C_6H_4{<}{}^{CO\text{———}}_{C(:NBr_3)}{>}N\cdot C_6H_4Br$, brown needles, which reddens at 180°, loses bromine, and yields *bromoiminophthalbromoanil*, $C_{14}H_8ON_2Br_2$, m. p. 242°, colourless leaflets. C. S.

Compounds of the Propane Series. II. SIEGMUND GABRIEL (*Ber.*, 1911, **44**, 3084—3091. Compare this vol., i, 644).—When heated at 200° and then distilled under diminished pressure, α-phthaliminoisobutyryl chloride loses carbon monoxide and hydrogen chloride, yielding *β-phthaliminopropylene*, $C_8H_4O_2:N\cdot CMe:CH_2$. This crystallises from alcohol in lustrous, hexagonal needles, m. p. 105—106°, and is hydrolysed by dilute acids to phthalic acid and acetone. It combines with bromine, forming *αβ-dibromo-β-phthaliminopropane*,

$$C_8H_4O_2:N\cdot CMeBr\cdot CH_2Br,$$

which forms lustrous, glassy needles, m. p. 86—89°, and, in the presence of moisture, decomposes into phthalimide and bromoacetone. When heated above its m. p. under diminished pressure, the dibromo-compound loses hydrogen bromide and yields a mixture of two isomeric *bromo-β-phthaliminopropylenes*, $C_8H_4O_2:N\cdot C:C_2H_3Br$, of which the one crystallises in leaflets or needles, m. p. 150—151°, whilst the other forms flat needles, m. p. 90—91°, with previous sintering at 86°. The interaction of bromine and *phthaliminoisobutyryl bromide* (obtained from phthaliminoisobutyric acid and phosphorus pentabromide) yields *dibromo-β-phthaliminopropylene*, $C_8H_4O_2:N\cdot C_3H_3Br_2$, which crystallises in lustrous needles, m. p. 169—170°; the same compound is obtained by the interaction of bromine and phthaliminoisobutyryl chloride.

Tribromo-β-phthaliminopropylene, $C_8H_4O_2:N\cdot C_3H_2Br_3$, obtained by the action of phosphorus and excess of bromine on phthaliminoisobutyric acid, crystallises in stout needles, resembling gypsum, m. p. 106—107°. It is hydrolysed by potassium hydroxide in aqueous alcoholic solution to a *dibasic acid*, $C_{11}H_9O_5N$. This crystallises in small needles, which become brown at 135° and decompose at

141—144°; the *silver* salt, $C_{11}H_7O_5NAg_2,1\frac{1}{2}H_2O$, and *barium* salt, $C_{11}H_7O_5NBa,3H_2O$, are described.

It is suggested that the above-mentioned tribromo-compound has the constitution $C_8H_4O_2\colon N\cdot C(CHBr_2)\colon CHBr$ or

$$C_8H_4O_2\colon N\cdot C(CH_2Br)\colon CBr_2,$$

whilst the dibasic acid has probably the formula

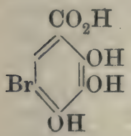
$$CO_2H\cdot C_6H_4\cdot CO\cdot NH(CO_2H)\colon CH_2.$$

When phthalimino*cyclo*propane (*loc. cit.*) is heated with excess of bromine on the water-bath, it yields a *tribromo*-derivative, $C_{11}H_6O_2NBr_3$, which crystallises in colourless needles, m. p. 162—163°, with previous softening at 159°, and is isomeric with the above tribromo-β-phthaliminopropylene. F. B.

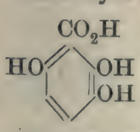
Preparation of 2 : 4-Diamino*iso*phthalic Acid and Derivatives. MARSTON TAYLOR BOGERT (D.R.-P. 236848).—Diacetyl-*m*-xylylene-4 : 6-diamine, m. p. 295° (compare Morgan, Trans., 1902, **81**, 93), when oxidised with potassium permanganate in the presence of magnesium sulphate yields 4 : 6-*diacetylamino*iso*phthalic acid*, colourless needles, m. p. 276°, which on hydrolysis with concentrated hydrochloric acid furnishes 4 : 6-*diamino*iso*phthalic acid hydrochloride* as yellow needles; the free *acid* is a colourless powder, m. p. 235° (decomp.); the *bisacetylanthranil* of the acid is crystalline, m. p. 283°, and forms with aniline (2 mols.) a condensation *product*, colourless needles, m. p. 315°. F. M. G. M.

Trihydroxybenzoic Acids. FRANZ VON HEMMELMAYR (*Monatsh.*, 1911, **32**, 773—791).—The influence of the position of the hydroxyl groups on the entry of bromine, and on the chemical behaviour of the substitution compounds obtained, has been studied in the case of the trihydroxybenzoic acids.

Phloroglucinolcarboxylic acid does not form a substitution compound, but on treatment with bromine, carbon dioxide is eliminated, and ultimately di- or tri-bromophloroglucinol is formed.



Pyrogallolcarboxylic acid forms a monobromo-derivative, which in view of the fact that it can be esterified, is considered to have the annexed constitution. Further treatment with bromine causes the elimination of carbon dioxide and subsequent formation of di- or tri-bromopyrogallol. The former is probably identical with a substance described by Einhorn (Abstr., 1904, i, 238).



The hydroxyquinolcarboxylic acid described by Thiele and Jäger (Abstr., 1901, i, 701) cannot be esterified by alcohol and hydrogen chloride. Accordingly, the annexed constitutional formula is the most probable. Only one bromine atom could be introduced, further action again causing elimination of the carboxylic group and formation of a dibromohydroxyquinol. The monobromo-compound could not be esterified.

The rate of elimination of carbon dioxide on boiling with water has been determined for each of these compounds; in general, the entry of the bromine atom doubles the rate of decomposition.

Dibromophloroglucinol forms colourless, lustrous needles, m. p. 171—172°; it dissolves in sodium carbonate or in ammonia with an orange-yellow coloration. *Dibromophloroglucinyl triacetate* forms colourless needles, m. p. 128—129°.

Monobromopyrogallolcarboxylic acid forms colourless or slightly yellow needles, which on heating sinter, decomp. 230°. The *barium* salt forms crystalline plates; the methyl ester separates in colourless needles, m. p. 135°. *Dibromopyrogallol* forms bunches of brown needles, which sinter at 160°, decomp. 173°. *Tribromopyrogallol* forms yellowish-brown plates, decomp. 180—186°.

The *barium* salt of hydroxyquinolcarboxylic acid separates in brown crystals. *Monobromohydroxyquinolcarboxylic acid* forms feather-like groups of needles, decomp. 199°. *Dibromohydroxyquinol* forms large, colourless, prismatic crystals. E. F. A.

Preparation of Tribasic Phenolphthalates. PHILIP A. KOBER and J. THEODORE MARSHALL (*J. Amer. Chem. Soc.*, 1911, **33**, 1779—1783).—In an earlier paper (this vol., i, 300), tripotassium phenolphthalate was described. An account is now given of the preparation of this salt and the corresponding trisodium salt,

$$\begin{matrix} CO_2Na\cdot C_6H_4 \\ ONa\cdot C_6H_4 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} C_6H_4\cdot ONa \\ OH \end{matrix},6H_2O,$$

which crystallises in rhombohedra, and is more soluble, but less stable, than the potassium salt. Of the three alkali atoms in these salts, two are readily displaced by the action of weak acids, such as acetic and carbonic acids, whilst the third, probably that attached to the carboxyl group, is more resistant, but is easily displaced by mineral acids. E. G.

Unsaturated δ-Ketonic Acids. ELMER P. KOHLER (*Amer. Chem. J.*, 1911, **46**, 474—502).—Unsaturated δ-lactonic acids have now been prepared for the first time. They can be readily obtained by the methods used for preparing the corresponding saturated compounds, or by introducing bromine into saturated ketonic acids and eliminating hydrogen bromide from the product.

Methyl γ-benzoyl-β-phenylethylmalonate can be obtained in good yield by the condensation of methyl malonate with phenyl styryl ketone in presence of piperidine; on hydrolysis, it yields the free acid. The *ethyl* ester, $CH_2Bz\cdot CHPh\cdot CH(CO_2Et)_2$, m. p. 65°, forms friable needles, and, on bromination, yields two stereoisomeric *ethyl γ-bromo-γ-benzoyl-β-phenylethylmalonates*, m. p. 88° and 43°, the former crystallising in needles and the latter in large prisms or tablets. The methyl ester similarly yields two *bromo*-derivatives, m. p. 113° and 87°, crystallising in needles and prisms respectively; on the addition of bromine to solutions of these compounds in carbon tetrachloride, two isomeric *methyl αγ-dibromo-γ-benzoyl-β-phenylethylmalonates*, m. p. 132° and 94°, are produced, which crystallise in needles and large tablets respectively.

Methyl γ-benzoyl-β-phenylvinylmalonate, $CHBz\colon CPh\cdot CH(CO_2Me)_2$, m. p. 94°, obtained by the action of potassium hydroxide on the methyl γ-bromo-γ-benzoyl-β-phenylethylmalonates, forms large, trans-

parent prisms or tablets; it does not combine with bromine, but yields a *bromo*-derivative, m. p. 141°, which crystallises in prisms or tablets. When methyl γ-benzoyl-β-phenylvinylmalonate is hydrolysed with potassium hydroxide, *mono*- and *di-potassium* salts are produced, which on treatment with acids yield *γ-benzoyl-β-phenylbutyrolactonic acid*, $\begin{array}{l}CH_2Bz\cdot CPh\cdot CH\cdot CO_2H\\ \qquad\; O\text{——}CO\end{array}$, which crystallises from water in small, lustrous pyramids containing $2H_2O$. When heated the hydrated acid melts at about 100°, then loses water, re-solidifies, and finally melts and decomposes at about 170°. The product of hydrolysis of the unsaturated ester contains also a small quantity of *δ-hydroxy-βδ-diphenylcrotolactonic acid*, $\begin{array}{l}OH\cdot CPh\cdot CH\colon CPh\\ \quad O\text{—}CO\text{—}CH\cdot CO_2H\end{array}$, m. p. about 170°, which crystallises in slender needles. When this acid is heated above its m. p., it is converted into benzoylphenylvinylacetic acid and *δ-hydroxy-βδ-diphenyl-δ-crotolactone*, $\begin{array}{l}OH\cdot CPh\cdot CH\colon CPh\cdot CH_2\\ \quad O\text{—————————}CO\end{array}$, m. p. 124°.

When benzoylphenylbutyrolactonic acid is heated at 170—185° until carbon dioxide ceases to be evolved, four substances are produced, namely: (1) γ-benzoyl-β-phenylvinylacetic acid; (2) an *acid*, m. p. 180°, isomeric with γ-benzoyl-β-phenylvinylacetic acid, and crystallising in large plates; (3) γ-benzoyl-β-phenyl-β-butyrolactone, and (4) a small quantity of an unsaturated *lactone*, probably $\begin{array}{l}CPh\cdot CH\colon CPh\\ CH\text{—}CO\text{—}O\end{array}$, m. p. 172°, which forms thin, lemon-yellow plates.

γ-Benzoyl-β-phenylvinylacetic acid, $CHBz\colon CPh\cdot CH_2\cdot CO_2H$, m. p. 135°, forms small, colourless prisms. When a solution of this acid in methyl alcohol is saturated with hydrogen chloride, *methyl β-chloro-γ-benzoyl-β-phenylbutyrate*, $CH_2Bz\cdot CPhCl\cdot CH_2\cdot CO_2Me$, m. p. 131°, is produced, which crystallises in slender needles. The unsaturated acid combines with bromine to form two stereoisomeric *βγ-dibromo-γ-benzoyl-β-phenylbutyric acids*, $CHBzBr\cdot CPhBr\cdot CH_2\cdot CO_2H$, which decompose without melting; one form crystallises in plates and the other in slender needles. When these dibromides are added to solution of sodium hydrogen carbonate, they are converted into a *lactone*, probably $\begin{array}{l}CHBz\cdot CPh\colon CH\\ O\text{—————}CO\end{array}$, m. p. 131°, which forms pale yellow needles.

γ-Benzoyl-β-phenyl-β-butyrolactone, $\begin{array}{l}CH_2Bz\cdot CPh\cdot CH_2\\ \qquad\quad O\text{——}CO\end{array}$, m. p. 93°, crystallises in needles or prisms, and is very stable; it is not affected when boiled with water or sodium carbonate solution, and does not decompose when heated at 200°. When the lactone is added to alcoholic potassium hydroxide, it is converted into γ-benzoyl-β-phenylvinylacetic acid, and if treated with methyl alcohol and hydrogen chloride, it is transformed into methyl β-chloro-γ-benzoyl-β-phenylbutyrate. If a solution of the lactone in glacial acetic acid is saturated with hydrogen bromide, *β-bromo-γ-benzoyl-β-phenylbutyric acid*, $CH_2Bz\cdot CPhBr\cdot CH_2\cdot CO_2H$, is produced, which forms long needles

and decomposes without melting. When an ethereal solution of γ-benzoyl-β-phenyl-β-butyrolactone is treated with magnesium ethyl bromide and the product is decomposed with water before the addition of acid, *δ-hydroxy-βδ-diphenyl-β-heptolactone*,

$$\begin{array}{l}OH\cdot CPhEt\cdot CH_2\cdot \underset{|}{C}Ph\cdot \underset{|}{C}H_2 \\ \qquad\qquad\qquad\qquad\quad O\text{——}CO\end{array},$$

m. p. 190°, is produced, but if the magnesium derivative is poured directly into a mixture of ice and hydrochloric acid, a *stereoisomeride*, m. p. 140°, is formed. On adding acids to solutions of the potassium salts of these lactones, a third *isomeride*, m. p. 150°, is obtained, which must be a δ-lactone.

γ-Bromo-γ-benzoyl-β-phenylbutyric acid, $CHBzBr\cdot CHPh\cdot CH_2\cdot CO_2H$, was obtained in two stereoisomeric forms by the action of bromine on benzoylphenylbutyric acid, one, m. p. about 189° (decomp.), which forms flat needles or plates, and the other, m. p. 145° (decomp.), which crystallises in small prisms; the corresponding *methyl* esters have m. p. 132° and 87° respectively. When these bromo-acids are dissolved in a solution of sodium carbonate, each is converted into a mixture of two stereoisomeric *γ-benzoyl-β-phenyl-γ-butyrolactones*,

$$\begin{array}{l}\underset{|}{C}HBz\cdot CHPh\cdot \underset{|}{C}H_2 \\ O\text{————————}CO\end{array},$$

one, m. p. 130°, forming large tablets, and the other, m. p. 98°, lustrous needles. *γ-Hydroxy-γ-benzoyl-β-phenylbutyric acid*,

$$OH\cdot CHBz\cdot CHPh\cdot CH_2\cdot CO_2H,$$

m. p. 160° (decomp.), obtained when either of the lactones is dissolved in alcoholic potassium hydroxide and subsequently acidified, forms long, colourless needles. By the action of magnesium ethyl bromide on the lactone of m. p. 130°, *γ-hydroxy-γ-benzoyl-β-phenyl-γ-heptolactone*, $\begin{array}{l}OH\cdot CPhEt\cdot \underset{|}{C}H\cdot CHPh\cdot \underset{|}{C}H_2 \\ \qquad\qquad\quad O\text{—————}CO\end{array}$, m. p. 103°, is produced, which crystallises in needles.

E. G.

peri-Naphthalideacetic Acid. HERMANN PAULY [with WILHELM WALTER] (*Ber.*, 1911, 44, 2785—2786. Compare Sachs and Brigl, this vol., i, 719).—This substance, $C_{10}H_6<\begin{smallmatrix}-O-\\CO\end{smallmatrix}>CH\cdot CH_2\cdot CO_2H$, was prepared by oxidation of naphthalidedimethyl ketone (Zink, Abstr., 1902, i, 159) with sodium hypobromite. It crystallises in rosettes of needles, m. p. 168·5° (bath previously heated), 158° (bath not previously heated). The *silver* salt, $C_{14}H_9O_4Ag$, forms microscopic laminæ.

R. V. S.

Preparation of Acyl Derivatives of o-Salicyloxybenzoic Acids. C. F. BOEHRINGER & SÖHNE (D.R.-P. 236196 and 237211).—When *o*-salicyloxybenzoic acid is treated with condensing agents (such as acetic anhydride), acyl derivatives of general formula

$$R\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$$

(R = an acyl group) are obtained, and the acetyl and ethylcarbonyl derivatives (Abstr., 1910, i, 386) have now been prepared by the

action of acetic anhydride and ethylchlorocarbonate respectively on salicyloxybenzoic acid.

o-*Benzoyloxy*-o-*benzoyloxybenzoic acid*, leaflets, m. p. 152°, was obtained by the action of benzoyl chloride on *o*-salicyloxybenzoic acid in aqueous alkaline solution, and o-*salicyloxybenzoyl carbonate*,

$$C_{29}H_{18}O_{11},$$

m. p. 192°, in a similar manner with carbonyl chloride.

The second patent states that the preparation of *o*-acyloxybenzoyloxybenzoic acids proceeds smoothly without the application of heat if the required *o*-acyloxybenzoic acid is left in contact with a tertiary amine during a long period. A solution of acetyloxybenzoic acid in pyridine was found after some days to contain *o*-acetyloxybenzoyloxybenzoic acid, and a dimethylaniline solution of ethylcarbonylsalicylic acid furnished *o*-ethylcarbonyloxybenzoyloxybenzoic acid. F. M. G. M.

Angeli-Rimini Reaction of the Aldehydes. LUIGI BALBIANO (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 245—249. Compare Paolini, this vol., i, 779; Tiffeneau, Abstr., 1910, i, 379).—The author now finds that the above reaction is given also by anisylacetone and other ketones, so that he no longer maintains the opinion that the substance obtained by the dehydration of anethole glycol is an aldehyde.

R. V. S.

[Solutions of Benzaldehyde and Hydrogen Cyanide in Water.] LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1911, 249, 510—511. Compare Abstr., 1909, i, 623).—A reply to Wirth, this vol., i, 875.

T. A. H.

Preparation of *o*-Nitrobenzaldehyde. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (D.R.-P. 237358).—When dilute aqueous solutions of salts of *o*-ω-dinitrotoluene are treated at a low temperature with potassium permanganate, they yield *o*-nitrobenzaldehyde according to the equation:

$$3NO_2\cdot C_6H_4\cdot CH:NO_2Na + 2KMnO_4 + H_2O = 3NO_2\cdot C_6H_4\cdot CHO + 3NaNO_2 + 2MnO_2 + 2KOH.$$

If the mixture is kept neutral or only slightly alkaline, a theoretical yield of pure *o*-nitrobenzaldehyde is produced. F. M. G. M.

Oxidation of *m*-Nitrobenzoylformaldehyde. WILLIAM L. EVANS and EDGAR JOHN WITZEMANN (*J. Amer. Chem. Soc.*, 1911, 33, 1772—1779).—In an earlier paper (Abstr., 1908, i, 338) an account has been given of the behaviour of *m*-nitrobenzoylcarbinol towards oxidising agents. The work has now been extended to the preparation and oxidation of *m*-nitrobenzoylformaldehyde.

The *osazone* of *m*-nitrobenzoylformaldehyde, m. p. 223°, forms dark red needles.

When the aldehyde is treated with potassium permanganate in neutral or alkaline solution, or with potassium ferricyanide, freshly precipitated silver oxide, or freshly precipitated mercuric oxide in presence of sodium hydroxide in each case, *m*-nitrobenzoic acid is the sole product of oxidation. In the absence of alkali hydroxide,

freshly precipitated silver oxide and mercuric oxide do not effect the oxidation of the compound at the ordinary temperature, but at 100° convert it into *m*-nitrobenzoic acid. When the aldehyde is treated with hot solutions of copper acetate or with alkali hydroxides, it is transformed into *m*-nitromandelic acid.

The results of these experiments and those recorded in the earlier paper (*loc. cit.*) indicate that *m*-nitrobenzoylcarbinol and *m*-nitrobenzoylformaldehyde behave similarly to the parent substances (compare Evans, Abstr., 1906, i, 269), but that they are more sensitive to reagents in the presence of alkali hydroxides. Moreover, the nitro-derivatives show a greater tendency to progress to the benzoic acid stage, yielding *m*-nitrobenzoic acid, than to give the possible intermediate compounds, namely, *m*-nitromandelic and *m*-nitrophenylglyoxylic acids. E. G.

Catalytic Conversion of 1-Methyl*cyclo*pentane-3-one into Methyl*cyclo*pentane. NICOLAI D. ZELINSKY (*Ber.*, 1911, **44**, 2781—2782).—Skita and Ritter (this vol., i, 272) have shown that the catalytic reduction of a number of substances containing six-membered rings is attended by the production of small quantities of the corresponding saturated cyclic hydrocarbons. The author finds that catalytic reduction of 1-methyl*cyclo*pentane-3-one with nickel at 150—160° yields a mixture of water, the alcohol, the ketone, and the hydrocarbon, whilst if the temperature is raised to 250°, methyl*cyclo*pentane is obtained in good yield. The fact that at this temperature no dehydrogenisation occurs marks the difference between the five-membered and the six-membered ring. R. V. S.

Catalytic Reduction in a Vacuum. NICOLAI D. ZELINSKY (*Ber.*, 1911, **44**, 2779—2780).—Reductions by means of hydrogen in the presence of nickel can be accomplished under reduced pressure. From 1 : 3-dimethyl-Δ^3-*cyclo*hexene-5-one at 200° and 75—80 mm., 1 : 3-dimethyl*cyclo*hexanone was obtained. From *iso*phorone at a pressure of 70—75 mm., the temperature of the nickel being 180°, dihydro-*iso*phorone was produced. R. V. S.

Synthesis of New Hydroaromatic Ketones. GEORGES DARZENS and H. ROST (*Compt. rend.*, 1911, **153**, 772—775. Compare Abstr., 1910, i, 856; 1907, i, 627).—A description of new ketones obtained by the action of an organomagnesium halides on acid chlorides at $-10°$. The products are purified from small quantities of tertiary alcohols through the agency of their semicarbazones.

cyclo*Hexoyl*cyclo*hexene*, $C_6H_{11}\cdot CO\cdot C_6H_9$, b. p. 136°/19 mm., forms a *semicarbazone*, m. p. 117—118°. n-*Butyryl*cyclo*hexane*,

$$C_6H_{11}\cdot CO\cdot C_3H_7,$$

b. p. 94°/13 mm., forms a *semicarbazone*, m. p. 153—154°.

The following acid chlorides were obtained by the action of thionyl chloride on the acids: cyclo*Hexeneacetyl chloride*, $C_6H_{11}\cdot CH_2\cdot COCl$, b. p. 98—100°/23 mm.; 2-*methyl*cyclo*hexeneacetyl chloride*, b. p. 104—105°/13 mm.; 3-*methyl*cyclo*hexeneacetyl chloride*, b. p. 95—96°/11 mm.; 4-*methyl*cyclo*hexeneacetyl chloride*, b. p. 109—110°/8 mm.; 4-*methyl*cyclo*hexylacetyl chloride*, b. p. 75°/7 mm.

1-Methyl-4-*tert.*-butyl*cyclo*hexanone (this vol., i, 290) condenses with ethyl chloroacetate, giving *ethyl hydroxy*-1-*methyl*-4-tert.-*butyl*cyclo-*hexaneacetate*, $C_4H_9 \cdot C_7H_{11}(OH) \cdot CH_2 \cdot CO_2Et$, b. p. 129—131°/3 mm. This has been converted into *ethyl* 1-*methyl*-4-tert.-*butyl*cyclo*hexene-acetate*, b. p. 136—139°/10 mm.; the corresponding *acid* has b. p. 174—177°/10 mm., and the *chloride*, b. p. 127—128°/8 mm. *Ethyl* 1-*methyl*-4-tert.-*butyl*cyclo*hexaneacetate* has b. p. 146—149°/14 mm.; the corresponding *acid* has b. p. 173—176°/12 mm., and the *chloride*, b. p. 134—136°/12 mm.

These new chlorides give rise to the following ketones when treated with magnesium methyl iodide: 1-*Acetonyl*cyclo*hexene*,

$$C_6H_9 \cdot CH_2 \cdot COMe,$$

b. p. 79—80°/11 mm.; *semicarbazone*, m. p. 176°. *Acetonyl*-2-*methyl*-cyclo*hexene*, b. p. 212°; *semicarbazone*, m. p. 170°. *Acetonyl*-3-*methyl*-cyclo*hexene*, b. p. 206—207°; *semicarbazone*, m. p. 154°. 1-*Acetonyl*-4-*methyl*cyclo*hexene*, b. p. 208°; *semicarbazone*, m. p. 160—161°. *Acetonylmethylbutyl*cyclo*hexene*, b. p. 135—136°/10 mm.; *semicarbazone*, m. p. 206°. W. O. W.

Action of the Chloroanhydride of *cyclo*Propanecarboxylic Acid on Benzene in Presence of Aluminium Chloride. Nicolai M. Kijner (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1163—1173).—The author has confirmed the formation of benzoyl*cyclo*propane by the decomposition of benzoyl*cyclo*propanecarboxylic acid (Perkin), and shows that this ketone is also obtained by the interaction of the chloroanhydride of *cyclo*propanecarboxylic acid and benzene in presence of aluminium chloride at 35—60°. Benzoyl*cyclo*propane, obtained by the latter method, gives a γ-benzoylpropyl bromide, m. p. 35°, whilst this compound when prepared from the benzoyl*cyclo*propane given by Perkin's method has m. p. 30·5°; this difference is not explained The action of potassium hydroxide on γ-benzoylpropyl bromide yields benzoyl*cyclo*propane.

m-*Nitrobenzoyl*cyclo*propane*, $NO_2 \cdot C_6H_4 \cdot CO \cdot CH{<}\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, separates from methyl alcohol in rectangular plates, m. p. 77°, and on reduction with tin and hydrochloric acid yields a crystalline *base*, m. p. 97—98°, the diazo-compound of which combines with naphthols, forming scarlet azo-colouring matters.

cyclo*Propylbenzylamine*, $NH_2 \cdot CHPh \cdot CH{<}\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, obtained by reducing the oxime of benzoyl*cyclo*propane in alcoholic solution with sodium, has b. p. 234·7—235°/749 mm., D_0^0 0·9996—1·0019, $D_0^{17.5}$ 0·9884, D_0^{20} 0·9843, n_D 1·5353—1·5360. The *hydrochloride*, m. p. 220—221°, *platinichloride*, $(C_{10}H_{11}NH_2)_2,H_2PtCl_6$, m. p. 177° (decomp.), and the *thiocarbamide*, $NHPh \cdot CS \cdot NH \cdot C_{10}H_{11}$, m. p. 124°, were prepared. Oxidation of the amine by means of permanganate yields benzoyl*cyclo*propane.

*Phenyl*cyclo*propylmethylcarbinol*, $OH \cdot CPhMe \cdot CH{<}\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, obtained by the interaction of benzoyl*cyclo*propane and magnesium methyl

iodide, has b. p. 241—242°/761 mm., 151—152°/51 mm., D_0^{20} 1·0316, n_D 1·5350.

*a-Phenyl-a-*cyclo*propylethylene*, $CH_2{:}CPh{\cdot}CH<\overset{CH_2}{\underset{CH_2}{|}}$, prepared by the action of acetic acid on the preceding compound, has b. p. 211—213°/758 mm., D_0^{19} 0·9553, n_D 1·5497, and gives a golden-yellow coloration with a drop of concentrated sulphuric acid. T. H. P.

Aromatic Amino-ketones. FRANZ KUNCKELL (*Ber. deut. pharm. Ges.*, 1911, 21, 419—456).—Various amino-ketones, in the form of their acetyl derivatives, have been prepared by heating acetanilide and an acyl halide with aluminium chloride in carbon disulphide and decomposing the resulting aluminium double compound with very dilute hydrochloric acid at 0°; the hydrolysis of the acetyl derivative is effected by 20% hydrochloric acid. It seems essential to success in the process that the acyl halide should have a b. p. exceeding 80—90°, or should be halogenated; for instance, the method fails with acetyl chloride or *iso*butyryl chloride, but yields good results with acetyl bromide or chloroacetyl chloride.

p-*Aminopropiophenone*, $NH_2{\cdot}C_6H_4{\cdot}COEt$, m. p. 140°, yellow needles, forms an *acetyl* derivative, m. p. 161°, *hydrochloride*, m. p. 225°, *sulphate*, m. p. 225°, *oxime*, m. p. 153°, and *ethyl carbamate*, m. p. 154°. It reacts with carbonyl chloride in benzene to form *di*-p-*propionylphenylcarbamide*, $CO(NH{\cdot}C_6H_4{\cdot}COEt)_2$, m. p. 271°, whilst its hydrochloride reacts with hot aqueous potassium cyanate to form p-*propionylphenylcarbamide*, m. p. 218°.

p-*Aminobutyrophenone*, m. p. 84°, colourless needles, forms an *acetyl* derivative, m. p. 142°, *hydrochloride*, m. p. 178°, *sulphate*, m. p. 216°, *ethyl carbamate*, m. p. 128°, and *benzoyl* derivative, m. p. 170°. p-*Butyrylphenylcarbamide* and *di*-p-*butyrylphenylcarbamide* have m. p. 194° and 235° respectively.

ω-Chloro-p-*acetylaminoacetophenone*, $NHAc{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Cl$, m. p. 212°, yields *p*-acetylaminobenzoic acid by oxidation, and forms the following derivatives in consequence of the reactivity of the chlorine atom: p-*Acetylaminophenyl phenoxymethyl ketone*,

$$NHAc{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}OPh,$$

m. p. 145°; p-*acetylaminobenzoylmethyl acetate*,

$$NHAc{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}OAc,$$

m. p. 162° (the hydrolysis of which yields p-*acetylamino-ω-hydroxyacetophenone*, m. p. 176°, *phenylhydrazone*, m. p. 223°); p-*acetylaminobenzoylmethylbenzoate*, m. p. 200—201°; and p-*acetylamino-ω-phthaliminoacetophenone*, $NHAc{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}N<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4$, m. p. 277°. By treatment with nitric acid, D 1·5, at 0°, ω-chloro-*p*-acetylaminoacetophenone yields *ω-chloro*-m-*nitro*-p-*acetylaminoacetophenone*, yellow crystals, m. p. 120°; *ω-chloro*-m-*nitro*-p-*aminoacetophenone*, m. p. 185°, obtained by its hydrolysis, yields *m*-nitro-*p*-aminobenzoic acid on oxidation. The bromination of ω-chloro-*p*-acetylaminoacetophenone in chloroform at 100° yields *ω-chloro*-2 : 5-*dibromo*-4-*acetylaminoacetophenone*, m. p. 137°, the oxidation of which by alkaline hydrogen peroxide yields 2 : 5-*dibromo*-4-*aminobenzoic acid*, m. p. above 350°;

this acid yields 2 : 5-dibromobenzoic acid and *p*-dibromobenzene by the successive elimination of the amino- and the carboxyl groups. *ω-Chloro*-p-*aminoacetophenone*, m. p. 146°, obtained by the hydrolysis of its acetyl derivative, forms a *hydrochloride* and *benzoyl* derivative, m. p. 177°. It reacts with potassium acetate and potassium benzoate respectively to form p-*aminobenzoylmethyl acetate*,

$$NH_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot O\cdot CO\cdot CH_3,$$

m. p. 135°, and the corresponding *benzoate*, m. p. 188°; the hydrolysis of the former yields p-*amino-ω-hydroxyacetophenone*,

$$NH_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot OH,$$

m. p. 165° (*phenylhydrazone*, m. p. 199°).

By bromination in glacial acetic acid at 70°, ω-chloro-*p*-acetylaminoacetophenone yields *ω-chloro-ω-bromo*-p-*acetylaminoacetophenone*,

$$NHAc\cdot C_6H_4\cdot CO\cdot CHClBr,$$

m. p. 162°, which is converted into *p*-acetylaminobenzoic acid by oxidation and into *ω-chloro-ω-bromo*-p-*aminoacetophenone*, m. p. 80·5° (*hydrochloride*, m. p. 182°), by hydrolysis. By diazotisation and treatment with cuprous cyanide, ω-chloro-*p*-aminoacetophenone yields p-*chloroacetylbenzonitrile*, $CN\cdot C_6H_4\cdot CO\cdot CH_2Cl$, m. p. 98—100°, which is converted into the corresponding *acid*, m. p. 210°, by hydrolysis.

Chloroacetyl chloride, *m*-chloroacetanilide, and aluminium chloride react in carbon disulphide to form ω-m-*dichloro*-p-*acetylaminoacetophenone*, $NHAc\cdot C_6H_3Cl\cdot CO\cdot CH_2Cl$, m. p. 146—147°, which has been converted successively into 2-chloro-4-aminobenzoic acid and 2-chloro-4-hydroxybenzoic acid, and yields by hydrolysis ω-m-*dichloro*-p-*aminoacetophenone*, m. p. 96—97° (*hydrochloride*, m. p. 178°). In a similar manner, chloroacetyl chloride and *m*-bromoacetanilide yield *ω-chloro*-m-*bromo*-p-*acetylaminoacetophenone*, m. p. 113°, which is converted into the *amino*-compound, m. p. 97—98° (*hydrochloride*, m. p. 180°), by hydrolysis and into 2-bromo-4-aminobenzoic acid by oxidation. Chloroacetyl chloride and *o*-acetotoluidide yield *ω-chloro-3-acetylamino-4-methylacetophenone*, $NHAc\cdot C_6H_3Me\cdot CO\cdot CH_2Cl$, m. p. 160°, which is converted by oxidation, hydrolysis, and diazotisation successively into o-*acetylamino*-p-*toluic acid*, m. p. 267—270° (decomp.), *o*-amino-*p*-toluic acid, and *p*-toluic acid; it yields *ω-chloro-ω-bromo-3-acetylamino-4-methylacetophenone*, m. p. 110°, by bromination in acetic acid, and reacts with potassium acetate or benzoate to form an *acetate*,

$$NHAc\cdot C_6H_3Me\cdot CO\cdot CH_2\cdot O\cdot CO\cdot CH_3,$$

m. p. 90°, or *benzoate*, m. p. 130°. The nitration of ω-chloro-3-acetylamino-4-methylacetophenone yields a *nitro*-compound, m. p. 204°, the constitution of which is proved by its conversion ultimately into *o*-nitro-*p*-toluic acid.

ω-Chloro-5-acetylamino-3-methylacetophenone, m. p. 145°, yields m-*chloroacetyl*-m-*toluidine*, m. p. 132°, by hydrolysis. C. S.

α-Amino*iso*butyrophenone, $NH_2\cdot CMe_2\cdot COPh$. SIEGMUND GABRIEL (*Ber.*, 1911, 44, 3091—3092).—When kept for three weeks, α-amino*iso*butyrophenone (this vol., i, 212) is converted into a crystalline *substance*, $C_{30}H_{37}O_2N_3$, which separates from light petroleum in lustrous, glassy, flat, obliquely-cut needles or rhombohedral crystals,

m. p. 105—106°. An aqueous solution of the compound becomes strongly alkaline when boiled with water, owing to reconversion into the original amino-ketone. It dissolves in warm hydrochloric acid, yielding α-amino*iso*butyrophenone hydrochloride, which forms a *platinichloride*, $(C_{10}H_{13}ON)_2H_2PtCl_6$, m. p. 205—206°, with previous sintering at 195°. F. B.

Oxidation of Aniline. III. RIKŌ MAJIMA and YOSHIHIKO AOKI (*Ber.*, 1911, 44, 3080—3084. Compare this vol., i, 216).—By the oxidation of aniline with lead peroxide, Börnstein (Abstr., 1901, i, 375) obtained a compound, which he considered to be 2-amino-*p*-benzoquinonedianil. The compound is readily prepared by oxidising aniline in aqueous acetic acid solution at 0° with lead peroxide. Determinations of the molecular weight and analysis of its hydrochlorides show that it has the composition $C_{24}H_{20}N_4$, and not $C_{18}H_{15}N_3$. From its solubility in organic solvents, and the fact that it yields azophenine when heated with aniline in glacial acetic acid solution, the authors conclude that it has the constitution:

$$NPh{:}C{<}{\begin{matrix}CH{:}C(NHPh)\\C(NH_2){=}CH\end{matrix}}{>}C{:}NPh.$$

2-Amino-5-anilino-*p*-benzoquinonedianil forms a *monohydrochloride*, $C_{24}H_{20}N_4,HCl$, and a *dihydrochloride*, $C_{24}H_{20}N_4,2HCl,3H_2O$; the *acetyl* derivative, $C_{26}H_{22}ON_4$, crystallises in long, bluish-red prisms, m. p. 212°. F. B.

Binary Systems of which One Component is an Organic Compound and the Other an Inorganic Salt. BORIS N. MENSCHUTKIN (*J. Chim. Phys.*, 1911, 9, 538—558. Compare this vol., i, 65).—A résumé of the author's work since 1903 on the additive organic compounds of magnesium, aluminium, and calcium haloids. R. J. C.

Photochemical Reactions of the Nitrophenylindones. I. MARUSSIA BAKUNIN and E. LANIS (*Gazzetta*, 1911, 41, ii, 155—184).—4-Nitro-2-phenylindone, when kept in sunlight, yields a substance, m. p. 320—325° (decomp.), which has the same percentage composition and is very indifferent to chemical reagents. Solutions of 4-nitro-2-phenylindone in various solvents, when exposed to light, deposited crystalline substances (apparently mixtures) of different and inconstant melting points. From the ethereal solution three substances are produced, which cannot be separated by recrystallisation, but on melting the mixture of all three the substance of m. p. 218° is converted into 4-nitro-2-phenylindone, which can be removed. From the remainder, two substances can be obtained, one having m. p. 280°, and the other m. p. about 320°; the latter is identical with the substance obtained from 4-nitro-2-phenylindone without a solvent. The products obtained in the case of other solvents were similar to the three just described.

6-Nitro-2-phenylindone remains unchanged in sunlight, but when its

solutions are exposed to light, mixtures of crystalline substances are produced. In the case of the benzene solution the product was separated into three substances, m. p. 227—229°, about 280°, and above 300° respectively.

In the formation of 4-nitro-2-phenylindone from 4-nitro-α-phenylcinnamic acid and phosphoric oxide in chloroform, a small quantity of a yellow, crystalline substance, m. p. 286°, is obtained.

R. V. S

Chloroiminoquinones. LEMUEL CHARLES RAIFORD (*Amer. Chem. J.*, 1911, 46, 417—456).—Stieglitz and Earle (Abstr., 1904, i, 39) have described stereoisomeric chloroimino-acid ethers, and Stieglitz and Peterson (Abstr., 1910, i, 323; this vol., i, 879) have prepared stereoisomeric chloroimino-ketones. In the present paper, an account is given of experiments undertaken with the object of determining whether stereoisomerism could be observed in the chloroiminoquinones. Six chloroiminoquinones of a structure which should admit of the formation of stereoisomerides have been studied, but in no case was stereoisomerism discovered.

2-*Bromo*-4-*aminophenol*, m. p. 165°, crystallises in pale brown needles; its *hydrochloride* darkens at 225°, but does not melt.

2-*Bromo*-4-*chloroiminoquinone*, $O:C_6H_3Br:NCl$, prepared by the action of hypochlorous acid on 2-bromo-4-aminophenol, forms yellow crystals, and decomposes at about 60°.

2-*Chloro*-6-*bromo*-4-*aminophenol*, m. p. 181°, obtained by reducing the corresponding nitrophenol with stannous chloride, crystallises in thin plates, and is probably identical with the compound obtained by Clark (Abstr., 1893, i, 321). 2-*Chloro*-6-*bromo*-4-*chloroiminoquinone*, m. p. 87—88°, forms yellow crystals.

2 : 4 : 6-*Trichloro*-m-*cresol*, m. p. 47°, prepared by the action of sodium hypochlorite on *m*-cresol, crystallises in colourless plates, and on oxidation is converted into 2 : 6-dichlorotoluquinone; the *acetate*, b. p. 273—274°, was obtained as a colourless, viscous liquid.

When a solution of 2 : 4 : 6-tribromo-*m*-cresol in glacial acetic acid is treated with sodium nitrite, 2 : 4-dibromo-6-nitro-*m*-cresol, m. p. 134° (decomp.), and 2 : 6-dibromo-4-nitro-*m*-cresol, m. p. 87°, are obtained in yields of 35% and 40% respectively. 2 : 4-Dibromo-6-amino-*m*-cresol has m. p. 176°; the corresponding *benzoylamino*-compound, m. p. 198°, forms colourless crystals. 2 : 4-*Dibromo*-3-*hydroxy*-o-*tolyl*-6-*urethane*, $OH\cdot C_6HMeBr_2\cdot NH\cdot CO_2Et$, m. p. 155°, obtained by the action of ethyl chlorocarbonate on 2 : 4-dibromo-6-amino-*m*-cresol in presence of sodium hydroxide, is a brown solid. 2 : 6-*Dibromo*-4-*chloroiminotoluquinone*, $O:C_6HMeBr_2:NCl$, m. p. 86°, forms yellow, hexagonal plates. 2 : 6-*Dibromo*-4-*amino*-m-*cresol*, m. p. 116—117°, crystallises in brown scales; its *hydrochloride* is described. 2 : 6-*Dibromo*-4-*benzoylamino*-m-*tolyl benzoate*, m. p. 188°, forms colourless crystals. 2 : 6-*Dibromo*-3-*hydroxy*-p-*tolyl*-4-*urethane* has m. p. 169°. 2 : 6-*Dibromo*-4-*acetylamino*-m-*tolyl acetate*, m. p. 216°, crystallises in long, silky needles. When 2 : 6-*dibromo*-4-*nitro*-m-*tolyl ethyl carbonate*, $NO_2\cdot C_6HMeBr_2\cdot O\cdot CO_2Et$, m. p. 43—45°, obtained by the action of ethyl chlorocarbonate on 2 : 6-dibromo-4-nitro-*m*-cresol in presence of

sodium hydroxide, is reduced with tin and hydrochloric acid, it is converted into 2 : 6-dibromo-3-hydroxy-*m*-tolylurethane.

Kehrmann and Tichvinsky (Abstr., 1899, i, 129) have shown that 4-chlorotoluquinoneoxime exists in two modifications, which, on reduction, give a chloroaminocresol, m. p. 204—205°, identical with that obtained by the reduction of the substance produced by chlorinating 6-nitro-*m*-cresol in glacial acetic acid solution. Attempts have been made to prepare stereoisomeric chloroiminoquinones corresponding with these oximes. A chloroaminocresol prepared from 6-nitro-*m*-cresol had m. p. 166—167°, and on oxidation gave a chloroiminoquinone, m. p. 87°, whilst that similarly obtained from Kehrmann's chloroaminocresol had m. p. 91°. It is shown that these compounds are 2-*chloro-* and 4-*chloro*-6-*chloroiminotoluquinone* respectively.

4-*Chloro*-6-*benzoylamino*-m-*tolyl benzoate*, m. p. 220°, prepared from Kehrmann's chloroaminocresol, forms nearly colourless crystals. 4-*Chloro*-6-*chloroiminotoluquinone*, $O{:}C_6H_2MeCl{:}NCl$, m. p. 91°, obtained by the action of hypochlorous acid on Kehrmann's chloroaminocresol, crystallises in radiating needles.

4-*Chloro*-3-*chloroiminotoluquinone*, m. p. 65°, prepared in a similar manner from the chloroaminocresol obtained by the electrolytic reduction of 3-nitro-4-chlorotoluene, forms brown nodules.

When 2-*chloro*-6-*nitro*-m-*cresol*, $OH{\cdot}C_6H_2ClMe{\cdot}NO_2$, m. p. 133°, obtained by the chlorination of 6-nitro-*m*-cresol, is reduced with stannous chloride, it is converted into 2-*chloro*-6-*amino*-m-*cresol*, m. p. 166—167°, which forms colourless crystals; its *hydrochloride* darkens above 225°. The *acetate* of the corresponding *acetylamino*-compound has m. p. 178°. On oxidation, 2-chloro-6-amino-*m*-cresol yields o-*chlorotoluquinone*, m. p. 55°, which is readily reduced to o-*chlorotoluquinol*, m. p. 173°, crystallising in colourless leaflets. By the action of hypochlorous acid on 2-chloro-6-amino-*m*-cresol, 2-chloro-6-chloroiminotoluquinone, m. p. 87°, is obtained.

By the chlorination of *o*-nitrotoluene, a mixture of 2-chloro- and 4-chloro-6-nitrotoluene is produced. These compounds on electrolytic reduction are converted into 2-chloro- and 4-chloro-6-amino-*m*-cresol, which, on oxidation, yield *p*-chlorotoluquinone, m. p. 105°, and *o*-chlorotoluquinone, m. p. 55°. E. G.

[Preparation of Condensation Products from *p*-Benzoquinone or α-Naphthaquinone.] RUDOLF LESSER (D.R.-P. 236074).—When the condensation products of quinones (or other diketo-derivatives) are reduced in alkaline solution with sodium hyposulphite, valuable dyes are produced. The *products* from dianilino-*p*-benzoquinone, $C_6H_2O_2(NHPh)_2$, chlorodianilino-*p*-benzoquinone, and chloranilanilide (from aniline and chloranil) are mentioned. The *compound*, $C_6Cl_2O_2(NH{\cdot}C_6H_4{\cdot}OMe)_2$, obtained from chloranil and *p*-anisidine, forms red needles with metallic lustre, and the *product*,

$$C_{10}H_5O_2{\cdot}NH{\cdot}C_6H_4{\cdot}OEt,$$

from *p*-phenetidine and α-naphthaquinone, glistening, metallic, reddish-brown needles. F. M. G. M.

The Partial or Total Replacement of Halogens by Hydrogen in Polyhalogenated Aminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 236604).—When polyhalogenated aminoanthraquinones or their derivatives are treated with reducing agents (such as iron and acetic acid) in the presence of pyridine, one or more of the halogen atoms are displaced by hydrogen.

Under these conditions, 2 : 4-dibromo-1-aminoanthraquinone yields 2-bromo-1-aminoanthraquinone ; 2 : 4-dibromo-1-methylaminoanthraquinone furnishes 2-bromo-1-methylaminoanthraquinone, and 1 : 3-dibromo-2-aminoanthraquinone gives 3-*bromo*-2-*aminoanthraquinone* in brownish-yellow, glistening leaflets. F. M. G. M.

Preparation of *p*-Dialkylaminobenzyl-1-aminoanthraquinone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 236769).—When a mixture of 1-aminoanthraquinone and a tertiary aromatic amine is treated with formaldehyde, it yields a *p*-dialkylaminobenzyl-1-aminoanthraquinone of the general formula

$$C_6H_4{<}{}^{CO}_{CO}{>}C_6H_3{\cdot}NH{\cdot}CH_2{\cdot}C_6H_4{\cdot}NR_2.$$

p-*Dimethylaminobenzyl*-1-*aminoanthraquinone*, $C_{23}H_{20}O_2N_2$, obtained when dimethylaniline is employed, has m. p. 211°, and forms orange-red crystals, whilst p-*diethylaminobenzyl*-1-*aminoanthraquinone*, m. p. 196°, crystallises from xylene in red prisms. F. M. G. M.

Preparation of Mixed Arylanthraquinonylcarbamides. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 236979 and 236981).—Arylanthraquinonylcarbamides have previously been prepared ; it is now found that the reaction takes place when arylcarbamyl chlorides react with aminoanthraquinones. The *product* obtained by boiling a nitrobenzene solution of 2-aminoanthraquinone with diphenylcarbamyl chloride in the presence of sodium acetate forms yellow crystals, which does not fuse below 300° ; this reaction is capable of wide extension. The second patent states that when β-aminoanthraquinone is heated with phenylurethane, a yellow powder separates from the cooled mixture, which has the properties of *phenyl-β-anthraquinonylcarbamide*. F. M. G. M.

Conversion of 1 : 2-Benzanthraquinone (Naphthanthraquinone) into Anthraquinone-1 : 2-dicarboxylic Acid. ROLAND SCHOLL and EMIL SCHWINGER (*Ber.*, 1911, **44**, 2992—2998).—*Anthraquinone*-1 : 2-*dicarboxylic acid*, $C_6H_4{<}{}^{CO}_{CO}{>}C_6H_2(CO_2H)_2$, required for the synthesis of 1 : 2-phthaloylanthraquinone, has been obtained by the oxidation of 1 : 2-benzanthraquinone. By oxidation by potassium permanganate in neutral solution, diphthalylic acid and anthraquinone-1 : 2-dicarboxylic acid are both formed, but only in small amount (compare Graebe and Peter, Abstr., 1905, i, 704). However, when a 5% solution of 1 : 2-benzanthraquinone in concentrated sulphuric acid is added to twice the weight of hot water and the nearly boiling mixture is oxidised by solid potassium permanganate, anthraquinone-

1 : 2-dicarboxylic acid is formed in 75·5% yield. The same acid is obtained in about 22% yield when the oxidation is effected by nitric acid, D 1·15, at 190—195°.

Anthraquinone-1 : 2-dicarboxylic acid crystallises in pale yellow needles containing H_2O, yields anthraquinone by distillation with calcium oxide and a little water, and changes at its m. p., 267—268°, into the *anhydride*, $C_{16}H_6O_5$, m. p. 319—321°, yellow prisms and leaflets, which is converted by ammonia at 225—235° into the *imide*, m. p. 293°, yellow needles. C. S.

Relation between Bisnitroso-compounds and Arylnitroso-hydroxylamines. EUGEN BAMBERGER (*Ber.*, 1911, 44, 3066—3072). —According to Piloty (Abstr., 1902, i, 734) the colourless, bimolecular *C*-nitroso-compounds and the coloured, unimolecular nitroso-compounds are to be considered as belonging to the same class.

This view is supported by the author, who finds that chloroform, benzene, and glacial acetic acid solutions of certain typical bimolecular nitroso-compounds (bisnitrosylbenzyl, *d*-bisnitrosocarone, *iso*safrol-ψ-nitrosite, and anethole-ψ-nitrosite) acquire a blue or bluish-green colour when heated, and accordingly must contain the nitroso-compound in the unimolecular form.

An explanation is also given of the transformation of bisnitroso-carone, by the action of hydrochloric acid, into chlorocarone and caronebisnitrosylic acid (caronenitrosohydroxylamine) observed by Baeyer (Abstr., 1895, i, 379).

The first stage in the action consists in the dissociation of bisnitroso-carone into the unimolecular form, which under the influence of hydrogen chloride is converted into chlorocarone and nitroxyl: $C_{10}H_{15}O{\cdot}NO + HCl = C_{10}H_{15}OCl + NOH$. The latter compound then unites with a second molecule of the nitroso-compound to form caronebisnitrosylic acid, $C_{10}H_{15}O{\cdot}N(OH){\cdot}NO$.

The evanescent blue coloration observed on acidifying an alkaline solution of nitroethane is considered by the author to be due to the formation of either nitrosoethyl alcohol, NO·CHMe·OH, or the ψ-nitrile, NO_2·CHMe·NO. F. B.

Transformations of Thujane. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1157—1163).—In the preparation of thujane by the oxidation of thujylhydrazine (this vol., i, 71), the purification of the latter by means of its hydrochloride may lead to the partial inversion of the thujylhydrazine, and hence of the thujane, if any excess of acid is present with the hydrochloride ; thus, it was found that the thujane from the pure thujylhydrazine had $[\alpha]_D$ +53·41°, whilst two preparations from the crude hydrazine had $[\alpha]_D$ +69·29° and +73·07° respectively.

When boiled with dilute sulphuric acid (1 : 6), thujane remains unchanged, whilst in a sealed tube the rotation is slightly lowered.

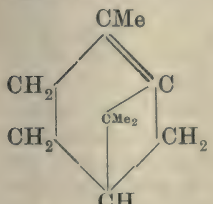
The action of hydrobromic acid on thujane for a short time yields an unstable bromo-derivative, but prolonged action gives a more stable, inactive *bromo*-compound, $C_{10}H_{19}Br$, b. p. 111—112°/19 mm., D_0^{20} 1·1812, n_D 1·4897, which is not decomposed when boiled with aqueous-alcoholic

potassium hydroxide. Reduction of this compound in 80% alcohol by means of a copper-zinc couple yields a *hydrocarbon*, $C_{10}H_{20}$, b. p. 157°/746 mm., D_0^{20} 0·7923, n_D 1·4377. The formation of this hydrocarbon, which is isomeric with menthane, indicates that the action of hydrobromic acid on thujane leads to the rupture of the trimethylene ring with formation of a *cyclo*pentane derivative, probably of the structure: $CHMe_2{\cdot}CBr{<}\begin{matrix}CH_2-CH_2\\ CHMe{\cdot}CHMe\end{matrix}$. As the stable and the unstable bromo-derivatives give one and the same unsaturated hydrocarbon on decomposition, it is to be assumed that they are structurally identical, and that the difference in stability depends on stereoisomerism of the cis- and trans-type.

The bromo-compound stable to alcoholic potassium hydroxide is decomposed by distillation with quinoline, giving the unsaturated, inactive *hydrocarbon*, $C_{10}H_{18}$, b. p. 162—164°/755 mm., D_0^{20} 0·8108, n_D 1·4527. The similar *hydrocarbon*, $C_{10}H_{18}$, obtained by the action of potassium hydroxide on the unstable bromo-derivative, has b. p. 163—164°/755 mm., $D_4^{18.5}$ 0·8131, n_D 1·4540, $[\alpha]_D$ +2·88°, whilst the isomeric hydrocarbon prepared by the action of potassium hydroxide on the iodo-compound has b. p. 162·5—163·5°/751 mm., D_0^{20} 0·8111, n_D 1·4527, $[\alpha]_D$ +0·2°. Each of these three hydrocarbons gives a raspberry-red coloration with acetic acid. These hydrocarbons are probably of identical structure, which should be one of the three following: $CMe_2{:}C{<}\begin{matrix}CH_2-CH_2\\ CHMe{\cdot}CHMe\end{matrix}$, $CHMe_2{\cdot}C{\lessdot}\begin{matrix}CH_2-CH_2\\ CMe{\cdot}CHMe\end{matrix}$, and $CHMe_2{\cdot}C{\lessdot}\begin{matrix}CH-CH_2\\ CHMe{\cdot}CHMe\end{matrix}$.

Another isomeric *hydrocarbon*, $C_{10}H_{18}$, obtained by converting thujane into the dibromo-compound, $C_{10}H_{18}Br_2$, and decomposing the latter with aqueous-alcoholic potassium hydroxide, has b. p. 162—164°/760 mm., D_0^{20} 0·8163, n_D 1·4520, $[\alpha]_D$ +23·62°. T. H. P.

Catalytic Isomerisation of α-Pinene. NICOLAI D. ZELINSKY (*Ber.*, 1911, **44**, 2782—2784. Compare Zelinsky and Glinka, this vol., i, 870).—α-Pinene (obtained by fractionation of French turpentine) yields an isomeride when treated with hydrogen in presence of palladium black from palladium chloride. This *iso*pinene has b. p. 158·5—159·5°, D_4^{20} 0·8573, n_{20} 1·4641, $[\alpha]_D$ −38·09°. It does not absorb hydrogen chloride, and a nitrosochloride could not be prepared from it. The author supposes the substance to be produced by dehydrogenisation of the hydropinene first formed, and assigns to it the annexed formula.



The same α-pinene, however, when treated with hydrogen for four weeks under the pressure of the head of acid in a Kipp's apparatus and in the presence of palladium black from palladium ammonium chloride, yields pinene of b. p. 167·5—168°/748 mm. Hydrogenisation of lævorotatory pinene by Sabatier's method gave

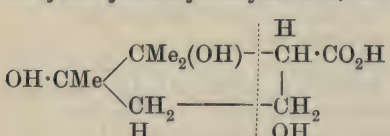
a hydropinene of b. p. 168—168·5° (corr.), D_4^{20} 0·8542, n_{20} 1·4601, $[a]_D$ −13·3°, and another *hydrocarbon*, $C_{10}H_{18}$, b. p. 163·5—165°/750 mm., D_4^{20} 0·8512, n_{20} 1·4580, $[a]_D$ −9·58°. R. V. S.

*iso*Laurolene. IWAN L. KONDAKOFF and I. SCHINDELMEISER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 992—1000).—Damsky (Abstr., 1888, 293) obtained *iso*laurolene by distilling the ammonium salt of sulphocamphylic acid in presence of ammonium chloride, but did not indicate the proportions of the two salts used. The authors have investigated this reaction, which they carried out in a current of carbon dioxide, and as molecular proportions of the two salts gave but little hydrocarbon, 2 mols. of ammonium chloride were taken per mol. of sulphocamphylate. The latter should be crystallised from 10% ammonia solution to prevent hydrolysis.

Sulphocamphylic acid, obtained by the action of sulphuric acid on camphoric anhydride, gave m. p. 162—164°, the value 160—165° having been given by earlier workers.

The products obtained by distilling the mixture of ammonium chloride and sulphocamphylate were: *iso*laurolene; di*iso*propenyl; a ketone giving an oxime, m. p. 116—118°, and a bromide, softening at 76°, m. p. 79°; β-hydroxyhexahydro-xylic acid (compare Lees and Perkin, Trans., 1907, **79**, 332), and possibly other cyclic hydrocarbons.

The reactions probably proceed as follows: The sulphocamphylic acid combines with the hydrogen chloride yielded by dissociation of the ammonium chloride, giving two compounds, which lose hydrogen chloride, with formation of α- and β-campholytic acids. The former of these readily undergoes isomeric change into the latter, which loses carbon dioxide and gives *iso*laurolene. These two acids may also be transformed, by way of their hydrochlorides, into campholactones, including ψ-campholactone; this then gives (1) the lactone of *cis*hydroxyhexahydroxylic acid, and from it the corresponding acid, and (2) xylic acid. The hydroxy-acids corresponding with the campholactones, and, to some extent, the acid corresponding with ψ-campholactone, in consequence of hydration, dehydration, and loss of carbon dioxide and other groups, give a pinacone (annexed scheme), this pinacone then undergoing dehydration to di*iso*propenyl. These hydroxy-acids also probably give an isomeride of camphorone or the latter itself.



The various products obtained are being investigated. T. H. P.

Santene and its Hydrohalides. IWAN L. KONDAKOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1107—1116).—The author has previously (Abstr., 1910, i, 327) drawn the conclusion that, on loss of hydrogen chloride, true bornyl chloride and also fenchyl chloride do not yield methylenecamphene and methylenefenchene immediately, but that they give, firstly, a mixture of bornylene and cyclene, and fenchobornylene and fenchocyclene respectively, these then undergoing isomeric change into (1) methylenecamphene, *iso*-

cyclene, and *iso*camphene, and (2) fenchene, fenchocyclene, and *iso*fenchene. May (*Diss.*, Berlin, 1910) arrived at a similar conclusion. The present paper records certain observations made in the attempt to confirm the above statement experimentally.

Two natural santenes were employed: that from sandalwood oil (compare Müller, Abstr., 1900, i, 677), and that from the essential oil of the fir (compare Aschan, Abstr., 1908, i, 94), these two being regarded as identical and pure. It is found that, in the latter case, santene cannot be obtained pure by fractionation, since the lower fractions of the oil contain a hydrocarbon with a lower boiling point than santene, whilst the neighbouring fractions with higher boiling points contain camphene and pinene. The hydrocarbon of low b. p. distils at 105—110°, does not change in the air, and is not oxidised by permanganate solution; its nature is under investigation. A hydrocarbon, C_7H_{10} (?), with this b. p. was obtained by Müller (*loc. cit.*) by the dry distillation of calcium teresantalate, either alone or mixed with calcium acetate.

When treated with concentrated hydrochloric acid, the various fractions of fir-santene exhibit the following behaviour: (1) the fraction, b. p. 105—125°, is turned brown, and yields principally a black, caoutchouc-like mass, and hence very little chloro-derivative; (2) that with b. p. 125—142° is coloured yellow, owing to the admixture with that of lower b. p., and gives a chloro-compound liquid at the ordinary temperature, and (3) that boiling at 142—147° remains colourless, and yields a mixture of liquid and solid chloro-derivatives. The santene hydrochloride obtained is identical with norbornyl chloride, and consists of two isomerides, melting at 14° and 81° respectively, assuming the m. p. 81°, given by Müller and by Aschan, to be that of the pure isomeride. Using conditions for its preparation different from those of these authors, it is found that santene hydrochloride from santalol has a lower melting point than 81°. This hydrochloride, when pure, remains unchanged for a long time, but is converted into the isomeride with the lower melting point under the influence of hydrochloric acid.

Contrary to Semmler's statement, the hydrochloride with high melting point is very stable to concentrated alcoholic potassium hydroxide at the ordinary temperature. On the water-bath it undergoes only partial decomposition in five hours, whilst in a sealed tube at 170° it yields in the same space of time the two products: (1) an optically inactive *hydrocarbon*, C_9H_{14}, b. p. 138·5—142·5°, D^{18} 0·8714, n_D 1·46761, and (2) an ether, b. p. about 195°.

The action of concentrated hydrobromic acid on santalol-santene yields a solid hydrobromide, melting in some cases at 25° and in others at 18°, and gradually undergoing change into an inactive liquid *isomeride*, $C_9H_{15}Br$, b. p. 79—81°/8 mm., D^{18} 1·273, n_D 1·50573, which either corresponds with the hydrochloride of lower melting point or represents a mixture of the two isomerides.

When treated with concentrated alcoholic potassium hydroxide, both the liquid and solid hydrobromides yield a mixture of santene and the ether, b. p. 195°. The formation of this ether, in this and also in the preceding case, is regarded as due to condensation.

Oxidation of the santene from the hydrohalides by means of permanganate gives a hydrocarbon, b. p. 137·5—142·5°, santene glycol, and a small quantity of a fragrant-smelling substance. Oxidation of santene from santalol gives the glycol in larger proportion and more rapidly.

The acetyl derivative, C_9H_{15}·OAc, of the santenol synthesised from sandalol santene at the ordinary temperature has b. p. 85—89°/8 mm., D^{20} 0·9859, n_D 1·45929, and is optically inactive. T. H. P.

Action of Nitrosyl Chloride on the Essential Oil of Bupleurum fructicosum. Nitrosochlorides. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 190—196).—The previous attempts to prepare a nitrosochloride from the essential oil of *Bupleurum fructicosum* (Francesconi and Sanna, this vol., i, 896) by the method used by Wallach (Abstr., 1889, 1069) for carvene having been unsuccessful, the oil was separated into seventeen fractions by distillation in a vacuum, but the method yielded no better results when employed on the separate fractions. By modifying the procedure, however, by omitting the water and acetic acid, a nitrosochloride has been prepared from all the fractions. A well-cooled mixture of an alcoholic solution of the oil with amyl nitrite or ethyl nitrite is well stirred and treated with a saturated alcoholic solution of hydrogen chloride in drops. The crude *nitrosochloride*, $C_{10}H_{16}ONCl$, obtained is an unstable substance, and, although its m. p. and rotatory power are fairly constant, it is a mixture of at least two nitrosochlorides, termed α and β, which have very different solubilities in chloroform. The more soluble α-nitrosochloride has m. p. 101—102°, $[\alpha]_D$ – 175°; the β-nitrosochloride has m. p. 100—101°, $[\alpha]_D$ – 285°. R. V. S.

Essential Oil of Bupleurum fructicosum, Linn. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 230—233. Compare this vol., ii, 1025; Francesconi and Sanna, this vol., i, 658, 896).—In the present paper an account is given of the fractional distillation of 10 litres of the essential oil. Seventeen fractions were collected, and the results are given of their examination in respect to refractive index, rotatory power, density, percentage composition, acidity, saponification number, etc. R. V. S.

$\Delta^{1,5}$-Dihydrocuminaldehyde [and] β-Phellandrene in the Essential Oil of Bupleurum fructicosum. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 325—331. Compare preceding abstract).—It is shown that the dihydrocuminaldehyde previously obtained from the nitrosochloride from this essential oil is $\Delta^{1,5}$-dihydrocuminaldehyde. The terpene of the oil is β-phellandrene, although it has a greater rotatory power than this substance as obtained from other sources. It gives a nitrosochloride, which (like its nitrosite) has a rotatory power of opposite sign to its own, and decomposes with production of $\Delta^{1,5}$-dihydrocuminaldehyde.
R. V. S.

Champaca Oil. BENJAMIN T. BROOKS (*J. Amer. Chem. Soc.*, 1911, 33, 1763—1772).—The flowers of *Michelia champaca* yield 0·37% of an

essential oil, two specimens of which gave the following constants: D^{30}_{30} 0·9040 and 0·9107; n^{30}_{D} 1·4640 and 1·4688; ester number, 124 and 146; the ester number of the latter sample after acetylation was 199. The oil contains phenylethyl alcohol, cineole, *iso*eugenol, benzyl alcohol, benzoic and acetic acids, and a crystalline ketone, $C_{16}H_{20}O_5$, first described by Bacon (this vol., i, 73). This ketone has $[\alpha]^{30}_{D}$ $-82·5°$; the phenylhydrazone has m. p. 161°. By a study of the action of alcoholic potassium hydroxide on the ketone, it is shown that it is probably a succinic ester of ethyl alcohol and a ketonic alcohol, $C_{10}H_{12}O_2$, containing the group $-CH\!:\!CH\cdot CO-$, and may therefore be represented by the formula $CO_2Et\cdot CH_2\cdot CH_2\cdot CO_2\cdot C_{10}H_{11}O$.

The essential oil of *Michelia longifolia* differs considerably from that of *M. champaca*, and gives the following constants: D^{30}_{30} 0·897, n_D 1·4470, and ester number 180; its most characteristic constituent is methyl or ethyl α-methylbutyrate.

The flowers of both species of *Michelia* contain an oxydase, and it is suggested that to such enzymes the formation of aldehydes and ketones in essential oils is largely due. E. G.

Essential Oil of Santolina chamæcyparissus, L. I. LUIGI FRANCESCONI and P. SCARAFÌA (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 255—260).—The quantity of essential oil contained in the stem of the plant is small, but it is found in considerable quantity in the leaves. The extraction was effected by distillation in steam, and the yield varied from 0·2% to 1·15% of the material taken, the maximum being obtained just before flowering. The densities and the rotatory powers of the various products were not markedly different. The oil begins to distil at 176° at the ordinary pressure. At 15—20 mm., distillation was carried out from 94° to 111°, six fractions being collected. The earlier fractions contained a terpene, whilst in the later ones there are probably hydroaromatic oxygenated compounds. The saponification numbers showed the presence of an ester, and indications of the presence of ketones were obtained. The oil does not contain acids, alcohols, or phenols. R. V. S.

Essential Oil of Santolina chamæcyparissus, L. II. Action of Hydroxylamine. LUIGI FRANCESCONI and P. SCARAFÌA (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 318—324. Compare preceding abstract).—By the action of hydroxylamine hydrochloride on the essential oil in aqueous-alcoholic solution in the presence of sodium hydrogen carbonate, the following substances are produced: (1) the hydroxylamine-oxime of a ketone, $C_{10}H_{16}O$; (2) an oxime of the same ketone; (3) an oxime of another ketone; (4) a hydroxylamine; (5) terpenes and other unaltered substances.

The terpene, after fractionation, has b. p. 165—170°, and appears to contain one double linking.

When the product of the reaction is distilled with steam, the distillate contains the two oximes and the hydroxylamine. The oximes can be removed by acidifying and redistilling. The *hydroxylamine* crystallises in hexagonal laminæ, m. p. 62—64°. When oxidised with mercuric oxide it yields a *nitroso*-compound, which is a colourless, crystalline substance, m. p. 60—62°: fused or in solution it is blue.

The *oximes* are liquids which reduce Fehling's solution after they have been boiled with hydrochloric acid, and at the same time this hydrolysis leads to the production of one or more carbonyl compounds.

The *hydroxylamineoxime*, $OH\cdot NH\cdot C_{10}H_{17}\colon N\cdot OH$, obtained by crystallisation from the original reaction product, forms large prisms or thin laminæ, which on heating soften at 180—185° and melt at 190°; the liquid evolves gas and resolidifies, melting again at 260°. If the heating is slow, the conversion into the substance of m. p. 260° occurs directly, no previous fusion being observed. The hydroxylamineoxime does not reduce Fehling's solution, unless it has been boiled previously with hydrochloric acid. It does not react with aldehydes. By the action of nitrous acid, a *dioxime*, $C_{10}H_{16}(N\cdot OH)_2$, is obtained; it forms small, lustrous prisms, m. p. 268° (decomp.). The *dibenzoyl-dioxime* has m. p. 150—155°. When the hydroxylamineoxime is kept at 190—200° for an hour or more, the above dioxime is obtained, and in addition the *amino-oxime*, $NH_2\cdot C_{10}H_{17}\colon N\cdot OH$, which crystallises in colourless prisms, m. p. 150°. R. V. S.

Components of Essential Oils. Composition of the Essential Oils of Xanthoxylum aubertia (Evodia aubertia), and Xanthoxylum alatum. FRIEDRICH W. SEMMLER and E. SCHOSSBERGER (*Ber.*, 1911, 44, 2885—2890).—The oil of *Xanthoxylum aubertia* was divided into three fractions. Fraction 1, b. p. 70—80°/16 mm., comprised 2—3%, and has D^{20} 0·8248, n_D 1·4977, a_D +30°. It is probaby an aliphatic terpene. Fraction 2, b. p. 115—130°/16 mm., comprised 80—90%. On purification it had the following properties: b. p. 119—123°/9 mm., D^{20} 0·8781, n_D 1·499, $[a]_D$ −58°. It consists in part of a sesquiterpene, *evodene*, of the same type as limene; eugenol methyl ether is also present, and constitutes 40—60% of the crude oil. The third fraction is a solid, m. p. 85° (about 10% of the oil); it is phloroacetophenone dimethyl ether, $C_{10}H_{12}O_4$.

Xanthoxylum alatum.—The first fraction, b. p. 50—60°/9 mm., comprised 80% of the crude oil, and is possibly l-*sabinene*, but is provisionally termed *xanthoxylene*; it has D^{20} 0·84, n_D 1·47457, a_D −26°, and forms a *hydrochloride*, b. p. 83—87°/10 mm., D^{20} 0·959, n_D 1·4824, a_D −11°. The *hydrocarbon*, $C_{10}H_{18}$, obtained from this on reduction showed b. p. 52—58°/9 mm., D^{20} 0·8275, n_D 1·4582, a_D −17°. The ozonide on decomposition yielded an acid, b. p. 174—180°/10 mm. The corresponding *sabinene ketone* has b. p. 102—106°/14 mm., D^{20} 0·9612, n_D 1·47064, a_D +14°.

The second fraction, which only amounted to 5—10% of the crude oil, yields two semicarbazones, m. p. 210—211° and 221°. The former corresponds with cuminaldehyde.

The third fraction consisted of phloroacetophenone dimethyl ether, $CH{<}\begin{matrix}C(OH)\cdot C(COMe)\\ C(OMe){=\!=}CH\end{matrix}{>}C\cdot OMe$; it forms a monobromo-derivative, m. p. 187°, an acetyl derivative, m. p. 107°, and a methyl derivative, m. p. 103° (Schimmel & Co., *Report*, 1909; Abstr., 1909, i, 313).

E. F. A.

Apparently Reversible Character of the Vulcanisation Reaction of Caoutchouc by Sulphur. PAUL BARY and L. WEYDERT (*Compt. rend.*, 1911, 153, 676—678).—The free and combined sulphur in a sample of vulcanised caoutchouc was estimated, and the former removed by extraction with acetone, or else separated by removing the gum with xylene. After heating the product at 145° for eight hours, the caoutchouc was again analysed in the same way. The results show that ordinary vulcanised caoutchouc is an equilibrium mixture, and that combined sulphur is set free on diminishing the osmotic pressure of the free sulphur. The reaction of vulcanisation is represented as $C_{10}H_{16} + S_2 \rightleftarrows C_{10}H_{16}S_2$, but the numerical data obtained are not in agreement with the ordinary law of mass action, whatever hypothesis may be adopted as to the degree of polymerisation of the hydrocarbon. The conclusion drawn is that the hydrocarbon molecules having polymerised by union at the double linkings, on vulcanisation sulphur first becomes attached only to the terminal double linkings of a chain; further vulcanisation, therefore, can only occur after depolymerisation. W. O. W.

Preparation of Substances Resembling Caoutchouc. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 235686).—When compounds of the general type :C:C·C:C:, where the free valencies are saturated partly with hydrogen and partly with alkyl groups, are heated either in the presence or absence of condensing agents, they polymerise into substances like caoutchouc.

Piperylene, $CHMe{:}CH{\cdot}CH{:}CH_2$, when heated at 150° during twenty-four hours or at 90—100° during eight days, yielded a colourless, elastic *substance*, isomeric with natural caoutchouc.

Plastic masses of similar nature were obtained by heating δ-methyl-$\Delta^{\alpha\gamma}$-pentadiene, $CMe_2{:}CH{\cdot}CH{:}CH_2$, at 200° during twenty-four hours, also from tetramethylerythrene, $CMe_2{:}CH{\cdot}CH{:}CMe_2$, and from the substance $CH_2{<}{\begin{matrix}CH_2-CH\\CH_2{\cdot}CH_2\end{matrix}}{>}C{\cdot}CMe{:}CH_2$. F. M. G. M.

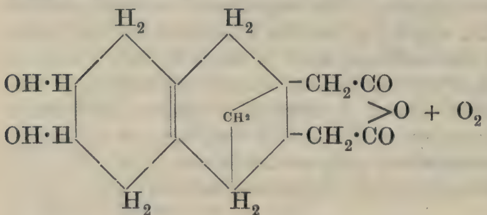
Clavicepsin, a New Glucoside from Secale cornutum. FRANCESCO MARINO-ZUCO and V. PASQUERO (*Gazzetta*, 1911, 41, ii, 368—374).—When *Secale cornutum* is extracted with hot alcohol for several days, the alcoholic solution contains a syrup partly soluble in water. From the aqueous solution, the new glucoside, $C_{18}H_{34}O_{16},2H_2O$, can be isolated in the form of acicular crystals, m. p. 91°, or, when anhydrous, 198°. It has $[\alpha]_D^{20}$ +142·27°. It is not hydrolysed by emulsin, but with acids it yields 2 mols. of dextrose (identified as phenylhydrazone) and 1 mol. of mannitol (identified by isolation and analysis) according to the equation: $C_{18}H_{34}O_{16} + 2H_2O = 2C_6H_{12}O_6 + C_6H_{14}O_6$. R. V. S.

Picrotoxin. FRANCESCO ANGELICO (*Gazzetta*, 1911, 41, ii, 337—349. Compare Abstr., 1910, i, 404, 577).—The action of hydriodic acid and phosphorus on either picrotin or picrotoxinin yields an acid, $C_{15}H_{18}O_4$, and a ketone, $C_{14}H_{16}O_3$, previously described. The reaction is accompanied by the evolution of carbon dioxide and a little carbon monoxide.

The action of alkaline permanganate on the acid $C_{15}H_{18}O_4$ gives (in addition to the acids $C_{15}H_{16}O_6$, $C_{13}H_{12}O_6$, and $C_{12}H_{12}O_7$) a small quantity of an *acid*, $C_{14}H_{16}O_6$, which forms small needles, m. p. 180°.

The acid $C_{13}H_{12}O_7$, m. p. 175°, is not a malonic derivative. When it is oxidised with chromic acid in the presence of 25% sulphuric acid, it yields a dibasic *acid*, $C_{12}H_{12}O_7$, which crystallises in needles, m. p. 289—290° (decomp.), and gives a *silver* salt, $C_{12}H_{10}O_7Ag_2$.

The series of acids which has now been obtained from picrotin and from picrotoxinin is therefore: $C_{15}H_{18}O_4$, $C_{15}H_{16}O_6$, $C_{14}H_{16}O_6$, $C_{13}H_{12}O_6$, $C_{13}H_{12}O_7$, and $C_{12}H_{12}O_7$. The author suggests the annexed formula for picrotin. Picrotoxinin would then be the unsaturated (hexahydronaphthalene) derivative containing no hydroxyl groups, but having also the two oxygen atoms of unknown function.



With a view to determining the function of these oxygen atoms, experiments have been made on various products with phosphorus pentachloride. The monocarboxylic acid, $C_{15}H_{18}O_4$, remains unaltered. The halogenated ketone yields an oily, chlorinated product, which gives a phenylhydrazone, and the halogenated ketone also yields a small quantity of a *substance*, m. p. 168—169°. The ketone, $C_{14}H_{16}O_3$, gives the same results, but in this case the substance of m. p. 168—169° was analysed, and corresponds with the union of 2 mols. of ketone less $1H_2O$, or $C_{28}H_{26}O_3Cl_2$. The ketone, $C_{14}H_{16}O_3$, when distilled with zinc dust gives traces of a substance, probably a *hydrocarbon*, of which the *picrate* has m. p. 205—206°.

The nitro-acid, $C_{13}H_{15}O_5N$ (compare Abstr., 1910, i, 578), is accompanied by a small quantity of a *substance*, m. p. 86—87°. When reduced with ammonium sulphide in the warm, the nitro-acid gives the corresponding *amino*-acid, $C_{13}H_{17}O_3N,H_2O$, m. p. 175—176°. The amino-acid is oxidised by permanganate at the ordinary temperature, giving a *tribasic acid*, $C_7H_{10}O_6$, which crystallises in small needles, m. p. 95°, and gives a *silver* salt, $C_7H_7O_6Ag_3$. R. V. S.

Composition of Tannin. WILHELM STEINKOPF and JOHANN SARGARIAN (*Ber.*, 1911, 44, 2904—2906).—Iljin (Abstr., 1909, i, 503) has stated that tannin derived from the commercial product by repeated purification has the composition 54·13% C and 3·22% H, values which are not in agreement with those usually obtained or with Nierenstein's formula. A careful repetition of Iljin's experiments indicates values 52·69% C and 3·77% H, in full agreement with those of previous observers. E. F. A.

Bile Pigments. II. Urobilinogen of Urine and the Nature of Ehrlich's Aldehyde Reaction. HANS FISCHER and FRIEDRICH MEYER-BETZ (*Zeitsch. physiol. Chem.*, 1911, 75, 232—261. Compare this vol., i, 803).—Urobilinogen has been prepared from pathological

urine in a crystalline form, and identified with hemibilirubin by the crystallographic characters. A number of unstable pyrrole derivatives, including all the crystalline blood pigments and the bile pigments at present known, are converted into urobilin on decomposition, both in experiments in test-tubes and in the organism. All these unstable pyrrole compounds contain a hydrogen atom attached to one of the carbon atoms in the chain, and they all give the Ehrlich reaction with *p*-dimethylaminobenzaldehyde.

The urobilinogen and urobilin tests are not decisive when they are given after unnatural substances have been administered to the animal; urobilinogen, moreover, may be present in urine in considerable quantity without giving the aldehyde reaction.

Ehrlich has shown that certain pathological urines give an intense red coloration with dimethylaminobenzaldehyde in acid solution. The dye in question is now shown to be a dipyrrylphenylmethane dye formed by a secondary reaction from the corresponding leuco-base.

Ethyl 2:5-dimethylpyrrole-3-carboxylate condenses with anisaldehyde to form a colourless, crystalline substance, $C_{26}H_{32}O_5N_2$, m. p. 199—200 (corr.).

The pyrrole derivative also condenses with *p*-dimethylaminobenz aldehyde in acid alcoholic solution to a colourless, crystalline leuco-base, $C_{27}H_{35}O_4N_3$, m. p. 239°. On oxidation with ferric chloride, the dye is obtained; it forms a hard, dark red, lustrous mass, with a green reflex. The colour is stable towards acids, but altered by sodium hydroxide, although restored again on making the solution acid. It has the properties of a triphenylmethane dye.

The corresponding dye from hemibilirubin and *p*-dimethylamino-benzaldehyde is reddish-violet and very sensitive to alkali; dilute sodium carbonate changes the violet colour into brownish-yellow.

E. F. A.

Bile Pigments. III. Hemibilirubin and its Oxidation Products. Hans Fischer and Paul Meyer (*Zeitsch. physiol. Chem.*, 1911, 75, 339—349. Compare Abstr., 1911, i, 803).—Hemibilirubin has been found to exist in two forms, an acidic and a non-acidic. The latter is the pure hemibilirubin. The former, which dissolves in solutions of hydrogen carbonates with the evolution of carbon dioxide, has not yet been obtained pure.

By the reduction of bilirubin in alkaline solution by means of sodium amalgam, three products have been obtained, namely: (I) hemibilirubin, (II) the acidic form of hemibilirubin, and (III) a substance which has not yet been identified. On oxidation all three substances yield the imide of hæmatic acid, together with methylethylmaleinimide. Hæmatic acid only was found among the products of the oxidation of bilirubin.

From determinations of molecular weight, the authors draw the conclusion that the formulæ previously ascribed to hemibilirubin are incorrect, and propose either $(C_{16}H_{22}O_3N_2)_2$ or $C_{33}H_{44}O_6N_4$.

H. W.

Melanin Pigments of Animal Origin. MAURICE PIETTRE (*Compt. rend.*, 1911, **153**, 782—785).—The material employed in this investigation was prepared by macerating sarcomatous tumours from horses, removing the cellular débris after cooling in ice, and separating the melanin pigment by centrifugation. When submitted to alkali hydrolysis the melanin yielded alanine, together with other crystalline amino-acids, the amount of which was insufficient for identification. The residual pigment had the composition C 61·72, H 4·39, N 9·4, S 1·6, Fe_2O_3 0·178%. Acid hydrolysis resulted in the separation of tyrosine (0·11%), leucine (2·95%), amorphous amino-acids (9·32%), and a pigment containing iron and sulphur, and having C 55·69, H 3·49, N 9·72%. The original melanin, therefore, appears to contain a protein group in union with a pigment.

W. O. W.

Action of Sulphurous Acid and of Sulphites on Various Dyes. HUGO WEIL, KARL DÜRRSCHNABEL and PAUL LANDAUER (*Ber.*, 1911, **44**, 3172—3179. Compare Dürrschnabel and Weil, Abstr., 1905, i, 947).—Methylene-blue is at first unchanged by sulphurous acid, but, after a time, a *substance* separates in small quantity in well-formed yellow crystals of both basic and acid character having the composition $C_{32}H_{36}O_8N_6S_5,5H_2O$ or $4\frac{1}{2}H_2O$, corresponding with the entry of three sulpho-groups into two methylene-blue residues. Characteristic derivatives could not be obtained; oxidation with dichromate gives a blue dye; with acetic anhydride a green, hygroscopic powder is obtained.

Sodium sulphite forms leucomethylene-blue, a lustrous, bronze-coloured, crystalline intermediate product being also formed, which probably represents methylene-blue sulphite.

With sodium hydrogen sulphite the first product is a dull blue precipitate, which, after remaining three or four days or on warming, is converted into the yellow, crystalline precipitate of leucomethylene-blue-sulphonic acid, $C_{16}H_{19}O_3N_3S_2,2H_2O$. If the original mother liquors are allowed to evaporate at a low temperature, very soluble, lustrous, silver platelets are obtained, which instantly become blue on exposure to the air; this is regarded as a sulphaminic acid.

Sulphurous acid and nitromethylene-blue interact to form a *nitro-leucomethylene-blue-sulphonic acid*, $C_{16}H_{18}O_5N_4S_2$; this has pronounced acid properties, and forms a green dye on oxidation. The mother liquors contain basic substances, which are oxidised to blue compounds. When the *nitro-leuco-acid* is reduced with zinc and hydrochloric acid, the *zinc* salt of an *aminoleuco-acid*, $ZnC_{32}H_{38}O_6N_8S_4$, is formed; this gives a blue oxidation product.

With Meldola's-blue, sulphurous acid yields a brown, crystalline compound, $C_{18}H_{16}O_4N_2S$.

Phenylindamine and sodium hydrogen sulphite form lustrous, colourless plates of a *substance*, $C_{12}H_{13}O_6N_3S_2$; tolylindamine and phenyltolylindamine behave similarly, the product in each case being a *leucodisulphonic acid*. Phenyltetramethylindamine reacts with sodium hydrogen sulphite or sulphurous acid to form lustrous, colourless crystals of a *monosulphonic acid*.

Safranines are not decolorised by sulphurous acid; coloured salts

separate after a time, which appear to be a mixture of sulphite and sulphate. E. F. A.

Action of a Mixture of Allyl Bromide and Furfuraldehyde on Magnesium: Synthesis of Furylallylcarbinol. A. SEMENTSOFF and P. KONJUKOFF-DOBRYNIA (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 990—992. Compare Javorsky, Abstr., 1908, i, 753).—*Furylallylcarbinol*, $\begin{matrix} CH{\cdot}CH \\ CH{-}{-}{-}O \end{matrix}\!\!>\!C{\cdot}CH(OH){\cdot}CH_2{\cdot}CH{:}CH_2$, prepared by the interaction of magnesium, allyl bromide, and furfuraldehyde, is a colourless liquid, b. p. 96—97°/21 mm., $D_4^{20\cdot5}$ 1·0424, $n_D^{20\cdot5}$ 1·49192, which rapidly turns yellow. T. H. P.

7-Methoxy-3 : 4-dihydro-1 : 4-benzopyrone. ALEXEI E. TSCHITSCHIBABIN and I. V. NIKITIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1185—1189).—7-Methoxy-3 : 4-dihydro-1 : 4-benzopyrone,

$$OMe{\cdot}C_6H_3{<}\begin{matrix} O{-}{-}CH_2 \\ CO{\cdot}CH_2 \end{matrix},$$

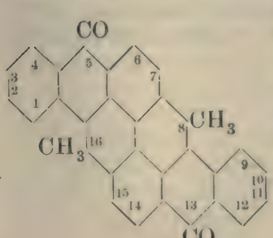
may be expected to lead to the formation of substances of the two structural formulæ which are at present regarded as the most probable for brazilin (compare Werner and Pfeiffer, *Chem. Zeitsch.*, 1904, 3, 421; Perkin and Robinson, Trans., 1908, i, 489; von Kostanecki and Lampe, Abstr., 1902, i, 481).

The synthesis of this compound is effected in two stages: (1) the action of the sodium derivative of *m*-methoxyphenol on sodium β-iodopropionate gives sodium β-*m*-methoxyphenoxypropionate, which (2) is converted into 7-methoxydihydrobenzopyrone by the action of phosphoric oxide. The condensation of the pyrone with veratraldehyde, which should give a compound having a structure closely related to the Pfeiffer-Perkin formula for trimethylbrazilin, is being investigated.

β-m-*Methoxyphenoxypropionic acid*, $OMe{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, separates from light petroleum in flat, shining needles, m. p. 82·5°; its *silver* salt was analysed.

3-*Methoxydihydrobenzopyrone*, $C_{10}H_{10}O_3$, crystallises from water in slender, colourless needles, m. p. 55°. T. H. P.

Synthetical Experiments in the Pyranthrone Series. ROLAND SCHOLL, JULIUS POTSCHIWAUSCHEG, and JOSEF LENKO (*Monatsh.*, 1911, 32, 687—710).—Pyranthrone homologues have been prepared in which the alkyl groups are attached to the benzene nuclei between the two anthraquinone complexes. 2 : 2′-Diethyl-1 : 1′-dianthraquinonyl condenses in a similar manner to the dimethyl compound (Scholl, Abstr., 1910, i, 271), although at a higher temperature, forming 8 : 16-dimethylpyranthrone (annexed formula), isomeric with 6 : 14-dimethylpyranthrone (Scholl, *loc. cit.*; this vol., i, 656, 676). 2 : 2′-Di-*n*-propyl-1 : 1′-dianthraquinonyl behaves similarly, but the isomeric di-*iso*propyldianthraquinonyl did not undergo condensation. The last can only react to give an aldol-like condensation product, and



the fact that none such is formed precludes the formation of aldol compounds as intermediate stages in the other condensations.

To prepare the 2-alkylanthraquinones, alkylbenzenes were condensed with phthalic anhydride in presence of aluminium chloride to 4-alkylbenzophenone-2′-carboxylic acids, these reduced to benzylbenzoic acids, condensed to alkylated anthrones, and oxidised to the corresponding anthraquinones.

In addition, *n*-propylbenzoylbenzoic acid was prepared by the Grignard reaction from *p*-iodo-*n*-propylbenzene, phthalic anhydride, and magnesium; it proved to be identical with the compound obtained by means of aluminium chloride, which in this instance does not cause isomerisation of the propyl group.

2-*n*-Propylanthraquinone could not be condensed to a homologue of the anthraflavone obtained from 2-methylanthraquinone (Bohn, Abstr., 1910, i, 405).

4-*Ethylbenzophenone-2′-carboxylic acid*, $CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_4Et$, separates in needles, m. p. 122°; it dissolves in concentrated sulphuric acid with a yellow coloration, changing to a reddish-brown on heating.

4-*Ethyldiphenylmethane-2′-carboxylic acid*, $CO_2H\cdot C_6H_4\cdot CH_2\cdot C_6H_4Et$, crystallises in colourless needles, m. p. 86°. Concentrated sulphuric acid rapidly converts it at the ordinary temperature into a mixture of 2-*ethylanthrone*-9 and 2-*ethylanthranol*-9. The desmotropic mixture consists of irregular, yellow crystals and yellow needles, m. p. 67—75°. When brominated in acetic acid and boiled with water, 2-*ethylanthraquinone* is obtained in yellow needles, m. p. 108°. It dissolves in sulphuric acid with a reddish-yellow coloration, becoming greenish-yellow when heated.

1-*Nitro*-2-*ethylanthraquinone* forms yellowish-brown needles or plates, m. p. 226°.

1-*Amino*-2-*ethylanthraquinone* is obtained on reduction in red needles, m. p. 153—154°.

1-*Iodo*-2-*ethylanthraquinone* crystallises in lustrous, small, yellowish-brown leaflets, m. p. 149°.

2 : 2′-*Diethyl*-1 : 1′-*dianthraquinonyl*,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2Et\cdot C_6H_2Et<\begin{matrix}CO\\CO\end{matrix}>C_6H_4,$$

prepared by heating the above iodo-compound with copper powder, crystallises in yellowish-brown prisms, m. p. 315°; in concentrated sulphuric acid it forms a yellow solution, which becomes violet-red on heating.

8 : 16′-*Dimethylpyranthrone* was obtained amorphous, m. p. much above 300°. It gives yellow solutions with a green fluorescence; the sulphuric acid solution is violet. It gives a deep violet, alkaline vat, which dyes cotton brownish-yellow.

4-n-*Propylbenzophenone-2′-carboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot C_3H_7,$$

crystallises in colourless needles, m. p. 125—126°.

4-n-*Propyldiphenylmethane-2′-carboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot C_3H_7,$$

forms slender needles, m. p. 80—81°.

The mixture of 2-n-*propylanthrone*-9 and 2-n-*propylanthranol*-9 is obtained in slender, yellow, microscopic needles, m. p. 60—61°, only partly soluble in dilute sodium hydroxide.

2-n-*Propylanthraquinone* forms yellow, slender needles, m. p. 98—99°, and dissolves in concentrated sulphuric acid with a reddish-yellow coloration.

1-*Nitro*-2-n-*propylanthraquinone* crystallises in yellow plates, m. p. 180°. 1-*Amino*-2-n-*propylanthraquinone* forms red, lancet-shaped crystals of metallic lustre, m. p. 172—173°.

1-*Iodo*-n-*propylanthraquinone* separates in lancet-shaped, lustrous, golden needles, m. p. 148—149°.

2 : 2′-*Di*-n-*propyl*-1 : 1′-*dianthraquinonyl* has m. p. 214—215°; the solution in concentrated sulphuric acid is brown, becoming dark green at about 80° and violet-red at about 220°.

8 : 16-*Diethylpyranthrone* is a yellowish-brown powder more soluble than the dimethyl homologue. The coloration with concentrated sulphuric acid is blue. It gives a deep reddish-violet alkaline vat, and dyes lighter shades than pyranthrone.

[With E. Böcker.]—4-iso*Propylbenzophenone-2′-carboxylic acid* forms lustrous, silky needles, m. p. 133—134°.

4-iso*Propyldiphenylmethane-2′-carboxylic acid* crystallises in platelets, m. p. 111°

The condensation product, 2-iso*propylanthrone*-9, was not isolated, but converted into 2-iso*propylanthraquinone*, which sublimes in concentrically grouped, yellow needles, m. p. 44—45°.

1-*Nitro*-2-iso*propylanthraquinone* forms yellow plates, m. p. 210—211°. 1-*Amino*-2-iso*propylanthraquinone* separates in red platelets or in needles with a green surface reflex, m. p. 146°.

1-*Iodo*-2-iso*propylanthraquinone* crystallises in well-formed bunches of yellow needles, m. p. 133—134°.

2 : 2′-*Di*-iso*propyl*-1 : 1′-*dianthraquinonyl* forms rhombohedric crystals, m. p. 326°. E. F. A.

Oxy-2-methylthiophens. Maurice Lanfry (*Compt. rend.*, 1911, **153**, 821—823).—The action of hydrogen peroxide on 2-methylthiophen is similar to that on thiophen (this vol., i, 740), and the products closely resemble those previously obtained, the oxygen being united to sulphur. *Dioxy-2-methylthiophen*, $C_5H_6O_2S$, has b. p. 168—170°/760 mm., D^{13} 1·25. *Tetraoxy-2-methylthiophen*, $C_5H_6O_4S$, has b. p. 187—189°/760 mm., D^{13} 1·37; on treatment with excess of bromine it forms *tribromotetraoxy-2-methylthiophen tetrabromide*, $C_5H_3O_4Br_3S,Br_4$, a yellow substance, m. p. −8°, decomposing on distillation. Fuming nitric acid converts the oxymethylthiophens into an ill-defined, yellow *polynitro*-derivative.

Excess of hydrogen peroxide converts 2-methylthiophen into a brown, amorphous substance. W. O. W.

Preparation of Amino- and Alkylamino substituted (in the Aryl Group) Derivatives of 3-Oxy-(1)-thionaphthen-2-carboxylic Acids and of 3-Oxy-(1)-thionaphthen. Kalle & Co. (D.R.-P. 237395).—When the *N*-substitution products of arylthio-

glycol-*o*-carboxylic acids (such as amino-, acylamino-, or alkylamino-acids) are fused with alkali hydroxides at about 170°, the fusion treated with water, and oxidised with potassium ferricyanide (or air), they furnish derivatives of "thioindigo."

3-*Acetylamino*-6-*carboxyphenylthiolacetic acid*,

$$NHAc \cdot C_6H_3(CO_2H) \cdot S \cdot CH_2 \cdot CO_2H,$$

a yellow powder, is prepared from monoacetyl-2 : 4-diaminobenzoic acid by successive diazotisation, xanthogenation, and treatment with chloroacetic acid; on fusion with sodium hydroxide it yields 6-*amino*-3-*keto*-(1)-*thionaphthen*-2-*carboxylic acid*, a grey, crystalline powder, which on boiling with hydrochloric acid furnishes 6-*amino*-3-*keto*-(1)-*thionaphthen*, a crystalline powder, and this by oxidation is finally converted into an "aminothioindigo" derivative.

4-*Acetylamino*-6-*carboxyphenylthiolacetic acid*, prepared in a similar manner from monoacetyl-2 : 5-diaminobenzoic acid, successively yielded 5-*amino*-3-*keto*-(1)-*thionaphthen*-2-*carboxylic acid*, 5-*amino*-3-*keto*-(1)-*thionaphthen*, yellow needles, and, finally, "*pp*-diaminothioindigo" in black flakes. F. M. G. M.

Anthraquinone-thioxanthone. FRITZ ULLMANN and ERNST KNECHT (*Ber.*, 1911, 44, 3125—3132. Compare Abstr., 1910, i, 270).—The colour change produced by the substitution of –S– for –NH– in the anthraquinoneacridones has been studied. Generally the result is the shifting of the colour into the yellow; thus the red anthraquinone-2 : 1-acridone corresponds with an orange anthraquinone-2 : 1-thioxanthone, and the isomeric orange 1 : 2-acridone compound corresponds with the yellow thioxanthone derivative.

Anthraquinone-*o*-thiolbenzoic acids were prepared by interaction of the appropriate chloro-derivatives with *o*-thiolbenzoic acid, and the former condensed by means of the *p*-toluenesulphonyl chloride or phosphorus pentachloride into anthraquinone-thioxanthones.

Anthraquinone-1-o-*thiolbenzoic acid*, $C_6H_4<\substack{CO\\CO}>C_6H_3 \cdot S \cdot C_6H_4 \cdot CO_2H$, crystallises in orange-yellow plates, m. p. 261° (corr.).

Anthraquinone-2 : 1-*thioxanthone*, $C_6H_4<\substack{CO\\CO}>C_6H_2<\substack{S\\CO}>C_6H_4$, forms lustrous, orange-red platelets, m. p. 346° (corr.). The solution in concentrated sulphuric acid is red.

Anthraquinone-2-*o*-thiolbenzoic acid has m. p. 278° (corr.), and not 271° as previously stated (*loc. cit.*). Anthraquinone-1 : 2-thioxanthone forms small, yellow needles, m. p. 278° (corr.); the azine crystallises in yellow, lustrous platelets.

1 : 5-*Dichloroanthraquinone* forms citron-yellow needles, m. p. 251° (corr.). It condenses very readily with *o*-thiolbenzoic acid to *anthraquinone*-1 : 5-*bis*-o-*thiolbenzoic acid*,

$$CO_2H \cdot C_6H_4 \cdot S \cdot C_6H_3<\substack{CO\\CO}>C_6H_3 \cdot S \cdot C_6H_4 \cdot CO_2H,$$

which crystallises in sealing-wax-red needles, m. p. 349° (corr.). It dissolves in alkali with an orange-red, and in concentrated sulphuric acid with a Bordeaux-red, coloration.

Anthraquinone-2 : 1 : 6 : 5-*bisthioxanthone*,

$$C_6H_4<{CO \atop -S-}>C_6H_2<{CO \atop CO}>C_6H_4<{CO \atop -S-}>C_6H_4,$$

forms red, lustrous platelets, which are not melted at 360°; they dissolve in concentrated sulphuric acid with a wine-red coloration.

1 : 8-*Dichloroanthraquinone* separates in yellow needles, m. p. 202°.

Anthraquinone-1 : 8-*bis-o-thiolbenzoic acid* forms orange-red crystals, m. p. 279° (corr.).

Anthraquinone-2 : 1 : 7 : 8-*bisthioxanthone* crystallises in Bordeaux-red, lustrous needles, giving a violet-red solution in concentrated sulphuric acid. E. F. A.

Preparation of Diglycollic Esters of Quinine. C. F. BOEHRINGER & SÖHNE (D.R.-P. 237450).—*Quinine diglycollate*,

$$O(CH_2\cdot CO_2\cdot C_{20}H_{23}ON_2)_2,$$

is prepared by treating a chloroform solution of quinine (11 parts) with diglycollic acid (3 parts) and allowing the mixture to remain during several days. It is a voluminous, tasteless, colourless powder, m. p. 70° (about), sparingly soluble in water, readily so in organic solvents.

Quinine diglycollyl sulphate, $C_4H_4O_3(C_{20}H_{23}O_2N_2)_2,H_2SO_4,3H_2O$, is obtained in crystalline form by treating a dichloroethylene solution of quinine with diglycollyl chloride in the same solvent and subsequently adding dilute sulphuric acid; the ester separates on the addition of sodium acetate.

The Grignard reaction with magnesium ethyl bromide, quinine, and diglycollic acid can also be employed for this preparation.

F. M. G. M.

Rearrangement of Quinine by Sulphuric Acid. BRUNO BÖTTCHER and STEFANIE HOROWITZ (*Monatsh.*, 1911, **32**, 793—796).—When quinine is heated at 100° with sulphuric acid, D 1·61, two bases, *A* and *B*, are formed; the former yields a soluble oxalate and sparingly soluble tartrate; the latter yields a sparingly soluble oxalate and a soluble tartrate.

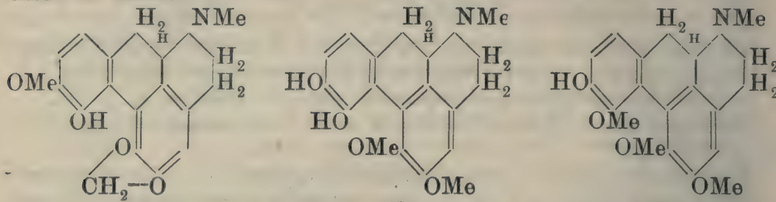
Base *A* crystallises in needles, m. p. 193·5° (corr.), $[\alpha]_D$ −237·89°; the solution in sulphuric acid fluoresces blue. The *sulphate* crystallises in bunches of needles, $[\alpha]_D$ −234·5°.

Base *B* forms colourless needles, m. p. 189° (corr.), $[\alpha]_D$ −181·67°; it is probably identical with Lippmann's *iso*quinine (Abstr., 1892, 82)

E. F. A.

Corydalis Alkaloids. IX. Corytuberine Sub-group. JOHANNES GADAMER (*Arch. Pharm.*, 1911, **249**, 503—510. Compare Abstr., 1902, i, 391; this vol., i, 483, and following abstract).—The author has undertaken with FRITZ KUNTZE a revision of the chemistry of the alkaloids forming this sub-group. The experimental results of this work, which will be published later, are discussed, and the following constitutional

formulæ for bulbocapnine (I), corytuberine (II), and corydine (III) are based on them:



(I.) (II.) (III.)

*iso*Corydine differs from corydine (III) only in the interchange of positions between –OMe and –OH in positions 3 and 4 in the phenanthrene nucleus. These formulæ are mainly based on the fact that in certain reactions these alkaloids show great similarity to *apo*morphine. Glaucine is the dimethyl ether of corytuberine (II). The two –OH groups in corytuberine are regarded as occupying positions 3 and 4, because (1) this alkaloid is readily oxidised by air in alkaline solutions, forming a dark green liquid. (2) The two hydroxyl groups in *apo*morphine occupy positions 3 and 4 in the phenanthrene nucleus, and the physiological action of corytuberine is very similar to that of *apo*morphine, whilst the characteristic emetic action disappears on methylation of these groups, as in bulbocapnine and corydine. (3) Bulbocapnine and *iso*corydine, like *apo*morphine, give Pellagri's reaction, so that they must contain a hydroxyl group in a position analogous to one of those in *apo*morphine, and as *iso*corydine is produced by methylation of corytuberine, the latter must also contain an –OH group similarly situated. Corytuberine itself does not give Pellagri's reaction, probably because it forms a betaine, in which the –OH group, which should function in Pellagri's reaction, is not available. T. A. H.

Corydalis Alkaloids. X. Bulbocapnine. JOHANNES GADAMER and FRITZ KUNTZE (*Arch. Pharm.*, 1911, **249**, 598–637. Compare Freund and Josephi, Abstr., 1894, i, 100; Herzig and Meyer, Abstr., 1898, i, 53, 389; Ziegenbein, Abstr., 1897, i, 175; Gadamer, Ziegenbein, and Wagner, Abstr., 1902, i, 391).—A historical résumé of work on bulbocapnine is first given, followed by a summary of the results, and analogies on which the new formula for bulbocapnine is based (preceding abstract).

In the mother liquors from the preparation of bulbocapnine, dehydrocorydaline was obtained (compare Schmidt, Abstr., 1909, ii, 85). On methylation with methyl sulphate or diazomethane, bulbocapnine yields a monomethyl ether, $C_{20}H_{21}O_4N$, m. p. 130—131°, $[\alpha]_D^{20}$ + 247·2° in chloroform, forming hemihedral, tetragonal crystals $[a:c = 1:1·0554]$, which gives a crystalline *sulphate*, $B_2,H_2SO_4,7H_2O$. On oxidation with iodine in alcohol this gives *dehydrobulbocapnine methyl ether hydriodide*, $C_{20}H_{18}O_4NI$, m. p. 228°, which with gold chloride gives the *aurichloride*, $C_{20}H_{17}O_4N,HAuCl_4$, crystallising in slender, cinnamon-brown needles, and on reduction with zinc dust in dilute sulphuric acid gives dl-*bulbocapnine methyl ether*, m. p. 136°,

forming rhombic crystals [$a:b:c=0{\cdot}87288:1:0{\cdot}61037$]. The latter on fractional crystallisation of the *d*-acid tartrate is separated into the optically isomeric methyl ethers.

On treatment with hot acetic anhydride, bulbocapnine yields a weakly basic diacetyl derivative, $C_{19}H_{17}O_4NAc_2$, which crystallises with $\frac{1}{2}$ mol. $C_2H_5{\cdot}OH$, a fact which explains Ziegenbein's assumption that this product is a triacetyl derivative (*loc. cit.*). On warming with potassium hydroxide in alcohol, this yields the *potassium* derivative of N-*acetylbulbocapnine* as a yellow, crystalline precipitate, which rapidly becomes brown in the air, and with alcohol and dilute sulphuric acid gives N-*acetylbulbocapnine*, m. p. 163—165°, crystallising in slender, red needles. With benzoyl chloride, by the Schotten-Baumann method, bulbocapnine gives a weakly basic *monobenzoyl* derivative, m. p. 202—203°, $[\alpha]_D^{20}$ + 92·7°, rhombic crystals [$a:b:c=0{\cdot}89437:1:0{\cdot}63116$], which forms a *methiodide*, m. p. 228—230° (decomp.), $[\alpha]_D^{20}$ + 28·1°, crystallising in rosettes of needles or silky leaflets, and on oxidation with iodine in alcohol gives *benzoyldehydrobulbocapnine hydriodide*, m. p. 219° (decomp.), $[\alpha]_D=0°$. The latter on reduction with zinc dust and sulphuric acid gives dl-*monobenzoylbulbocapnine*, m. p. 201—202°, and this on hydrolysis yields dl-*bulbocapnine*, m. p. 209—210°, which can be separated into its optical isomerides by crystallisation of the *d*-acid tartrate. With hot benzoyl chloride, bulbocapnine gives a *dibenzoyl* derivative, m. p. 156—157°, $[\alpha]_D$ = 0°, which on treatment with sodium hydroxide in methyl alcohol yields N-*benzoylbulbocapnine*, m. p. 160°. Oxidation of dibenzoylbulbocapnine with chromic acid did not give a crystalline quinonoid derivative such as is obtained with tribenzoyl*apo*morphine, although the red substance produced is probably a quinone.

With methyl iodide, bulbocapnine gives a methiodide (Freund and Josephi and Ziegenbein, *loc. cit.*), $[\alpha]_D^{20}$ +173·8° in alcohol, and the methyl ether on treatment with methyl iodide yields *bulbocapnine methyl ether methiodide*, $C_{20}H_{21}O_4N{\cdot}MeI$, m. p. 245—247°, $[\alpha]_D^{20}$ +163·7°.

Dimethylbulbocapnimethine, $C_{17}H_{13}O_4{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2$, best obtained by the method described by Pschorr for the analogous *apo*morphine compound (Abstr., 1906, i, 878), is a viscid, yellow liquid and is optically inactive; it furnishes an unstable *methiodide*,

$$C_{17}H_{13}O_4{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3I.$$

and a *methosulphate*, crystallising in thick, yellow needles. Either of these on warming with sodium hydroxide in methyl alcohol furnishes 3:4-*dimethoxy*-5:6-*methylenedioxy*-8-*vinylphenanthrene*, m. p. 101°, crystallising from ether in small, yellow needles. This on distillation with zinc dust gives ethylphenanthrene, which could not be obtained pure, but furnished a picrate, m. p. 138—140° (compare Pschorr, Abstr., 1906, i, 178), and on oxidation with permanganate in acetone yields the corresponding 3:4-*dimethoxy*-5:6-*methylenedioxyphenanthrene*-8-*carboxylic acid*, m. p. 228°, which crystallises in slightly red needles. The latter on further oxidation with permanganate in water gives (1) a soft mass, and (2) a *substance*, m. p. 247°, crystallising in red needles, which is probably dimethoxymethylenedioxyphenanthraquinonecarboxylic acid; it dissolved in alkalis,

forming eventually a colourless solution, from which acids liberate a colourless *substance*, m. p. 256—257°, which gradually becomes yellow on exposure to light. The soft mass referred to above, on solution in alcohol, deposits after a time a crystalline *substance*, m. p. 209°.

T. A. H.

Alkaloids of Ipecacuanha Root. OSKAR KELLER (*Arch. Pharm.*, 1911, 249, 512—524. Compare Paul and Cownley, Abstr., 1896, i, 192; Frerichs and Tapis, Abstr., 1902, ii, 711).—The bark of the root was extracted with ether, then moistened with ammonia solution, and re-extracted with ether and finally with chloroform. The first operation gave no alkaloid. The second furnished cephaëline and emetine, and the third psychotrine. Cephaëline crystallised from the second ethereal extract on concentration, and emetine was recovered from the mother liquors. Carthagena root yielded more cephaëline than Rio root. The colour reactions of both alkaloids are given (compare Allen and Scott-Smith, Abstr., 1903, ii, 117), and the dilutions at which they cease to be precipitated by the usual reagents.

Cephaëline softens at 93°, melts at 104—105°, and is readily soluble in alcohol or chloroform, less so in ether or light petroleum.

Emetine, $C_{30}H_{44}O_4N_2$, was obtained as a snow-white, amorphous powder; the *hydrochloride*, B,2HCl,$3H_2O$, crystallised in groups of needles and melted indefinitely, the *hydrobromide*, B,2HBr, in minute needles, and the *hydriodide*, B,2HI,$2H_2O$, m. p. 228—230°, in small masses of needles; the platinichloride, m. p. 248—249°, is amorphous. Emetine furnishes a *dibenzoyl* derivative, m. p. 96—106°, in which one benzoyl group is probably attached to a second nitrogen atom. It contains two methoxyl groups, and on heating with methyl iodide and sodium hydroxide forms a *methyl dimethiodide*, so that it appears to contain both a secondary and a tertiary nitrogen atom.

T. A. H.

Methyl Ether of Codeine and its Behaviour on Exhaustive Methylation. Morphine. XII. LUDWIG KNORR and PAUL ROTH (*Ber.*, 1911, 44, 2754—2758).—When α-chlorocodeide is heated in an autoclave for two days at 100—110° with sodium methoxide in methyl-alcoholic solution, codeine methyl ether is formed, and can be isolated as *hydrochloride*, $C_{19}H_{23}O_3N$,HCl, which crystallises (with $\frac{1}{2}$ mol. of alcohol) in needles, m. p. about 285° (previously sintering); $[\alpha]_D^{20}$ $-66°$ (in water). The *hydriodide*, $C_{19}H_{23}O_3N$,HI, crystallises in rosettes of needles, m. p. about 238—240° (decomp.). The *sulphate* (m. p. 241°), and the *nitrate* (which decomposes at 219°) also crystallise well. *Codeine methyl ether*, obtained from its salts, is a well crystalline substance, m. p. 137°, $[\alpha]_D^{15}$ $-80°$ (in alcohol, $c = 1{\cdot}965$). The *methiodide*, $C_{19}H_{23}O_3N$,MeI, crystallises in compact prisms, m. p. 270° (decomp.).

The methiodide, when boiled with sodium hydroxide, yields quantitatively a *methine base*, which is not crystalline; it suffers no rearrangement when heated with alcoholic potassium hydroxide (com-

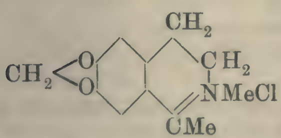
pare Knorr, Hörlein, and Grimme, Abstr., 1907, i, 956). The *hydriodide* (methylmorphimethine methyl ether hydriodide),

$$C_{20}H_{25}O_3N{\cdot}HI,$$

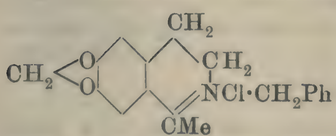
crystallises in needles or plates, m. p. about 204—208° (sintering from 200°), $[\alpha]_D^{15}$ $-85{\cdot}5°$ ($c=1{\cdot}4035$) or $-87{\cdot}3°$ ($c=1{\cdot}4950$). The *methiodide*, $C_{20}H_{25}O_3N{\cdot}MeI$, forms feathery crystals, m. p. 275°.

Methylmorphimethine methyl ether methiodide was deprived of iodine by means of silver oxide, and the resulting quaternary base was heated at 150° in a stream of hydrogen. Complete decomposition took place, and the following products were isolated and identified: ethylene, methylmorphenol, methyl alcohol, trimethylamine. R. V. S.

Preparation of 1-Aryl, Alkyl, or Alkylaryl Substituted Hydrastinines. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 235358. Compare Abstr., 1908, i, 901; this vol., i, 906).—When *N*-acyl derivatives of homopiperonylamines are submitted to the action of condensing agents, they furnish hydrastinine derivatives. When *acetylhomopiperonylamine*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NHAc$, colourless leaflets, m. p. 101°, is boiled with phosphoric oxide in toluene solution, it yields 6 : 7-*methylenedioxy*-1-*methyl*-3 : 4-*dihydro*iso*quinoline*; its *picrate*, a yellow, crystalline powder, has m. p. 232°; and the *methiodide*, yellow leaflets, m. p. 257°; when shaken during several hours with freshly precipitated silver chloride, it furnishes 1-*methylhydrastinine hydrochloride* (formula I), feathery needles, m. p. 232°.



(I.)



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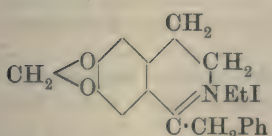


(III.)

When the foregoing *iso*quinoline derivative is treated with benzyl chloride it yields 2-*chloro*-6 : 7-*methylenedioxy-2-benzyl*-1-*methyl*-3 : 4-*dihydro*iso*quinoline* (formula II), yellowish-brown needles, m. p. 248°.

Phenacetylhomopiperonylamine, $CH_2{:}O_2{:}C_6H_3{\cdot}[CH_2]_2{\cdot}NH{\cdot}CO{\cdot}CH_2Ph$, yellow needles, m. p. 96°, under similar treatment yields 6 : 7-*methylenedioxy*-1-*benzyl*-3 : 4-*dihydro*iso*quinoline*, a yellow, oily liquid, b. p. 240°/16 mm.; its *picrate*, yellow crystals, has m. p. 189—190°, and the *methiodide*, yellow needles, m. p. 252°, on treatment with silver chloride furnishes 1-*benzylhydrastinine hydrochloride* (or *methochloride*), an uncrystallisable resin, readily soluble in water.

6 : 7 - *Methylenedioxy* - 1 - *benzyl*-3 : 4-*dihydro*iso*quinoline ethiodide* (formula III) forms yellow crystals, m. p. 214°.

Benzoylhomopiperonylamine, m. p. 122°, yields 6 : 7-*methylenedioxy*-1-*phenyl*-3 : 4-*dihydro*iso*quinoline*, colourless crystals, m. p. 142—143°; its *methiodide*, yellow needles, has m. p. 241°. F. M. G. M.

Strychnine and Brucine. [III.] ROBERTO CIUSA and G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 201—206. Compare Abstr., 1910, i, 583; this vol., i, 155).—By the action of bromine on strychnine, under the conditions employed by Löbisch and Schoop (Abstr., 1886, 267), the authors obtained a monobromostrychnine, m. p. 222—223°, identical with that formerly described by them; they consider, therefore, that the β-monobromostrychnine of Löbisch and Schoop does not exist.

When treated with bromine in glacial acetic acid, brucine yields a *perbromide*, $C_{23}H_{26}O_4N_2Br_3,H_2O$, crystallising in yellowish-white needles, which do not melt at 270°. From it a *monobromostrychnine platinichloride*, $(C_{23}H_{25}O_4N_2Br)_2,H_2PtCl_6,H_2O$, can be obtained.

On treating strychnine with potassium chlorate and hydrochloric acid in the cold, the tetrachlorostrychnine of Minunni and Ortoleva (Abstr., 1900, i, 309) is produced, together with an amorphous, isomeric *tetrachlorostrychnine*, $C_{21}H_{18}O_2N_2Cl_4,HCl,2H_2O$. When the cooling is omitted in the above reaction, an *octachlorostrychnine* is obtained as a yellowish-white, crystalline powder, which on analysis gives numbers corresponding approximately with the formula

$$C_{24}H_{14}O_2N_2Cl_8,3H_2O.$$

It yields a p-*nitrophenylhydrazone*, to which the formula

$$C_{24}H_{14}ON_2Cl_8{:}N_2H\cdot C_6H_4\cdot NO_2,3H_2O,$$

is ascribed.

The physiological action of the derivatives now and previously described has also been studied. The two dibromides, m. p. 122° and 260°, bromostrychnine, and the corresponding dibromide are as toxic as strychnine itself, whilst the octachlorostrychnine (like Minunni's tetrachlorostrychnine) and the acid, $C_{19}H_{22}O_6N_2$, are not toxic. R. V. S.

Iodine Derivatives of Strychnine, Brucine, and Some Other Alkaloids. L. KRAUZE (*Bull. Acad. Sci. Cracow*, 1911, [*A*], 6, 355—368).—True periodides of strychnine bases have been obtained by Buraczewski and Kozniewski (Abstr., 1908, i, 1007) and Kozniewski (Abstr., 1909, i, 826).

When more iodine is used, under otherwise similar experimental conditions, two modifications of a *strychnine heptaiodide*,

$$C_{21}H_{22}O_2N_2,HI,I_6,$$

are formed. One of these is obtained from solutions containing 10% excess of iodine in brownish-needles with a golden lustre, m. p. 151°; it soon decomposes when kept. The other is formed when considerably more iodine is used; it separates in hard, black prisms of a steel-like lustre, m. p. 176—177°, which are stable when kept. Both forms when warmed with alcohol or acetone are converted into Jörgensen's tri-iodide (*J. pr. Chem.*, 1870, [ii], 2, 1334).

By the action of an alcoholic iodine solution on di-iodostrychnine, a brown product is obtained containing more than three iodine atoms, which is a mixture, and could not be obtained crystalline. On warming with acetone, it becomes yellow, forming a new insoluble

di-iodostrychnine. Strychnine evidently tends to form several periodides, a property entirely lacking in brucine.

Buraczewski and Dziurzyński (Abstr., 1910, i, 873) have shown that complicated reactions take place on boiling di-iodostrychnine in acetone; two non-poisonous, crystalline products were obtained. These have now been studied more fully. The one forms small, silky needles, m. p. 281°, $C_{24}H_{27}O_3N_2I,1\frac{1}{2}H_2O$, the other yields hard prisms, m. p. 271°, $C_{24}H_{29}O_4N_2I,1H_2O$.

The former, *iodo-acetonylstrychnine*, $C_{21}H_{22}O_2NI\cdot CH_2\cdot COMe$, does not interact with acids or alkalis; with moist silver oxide a soluble, easily decomposed base is obtained; it reduces Fehling's solution and forms a *phenylhydrazone*, which is not well characterised. The *picrate* forms lustrous, yellow, silky needles; the *dichromate* is yellow and flocculent. It is optically inactive and does not react with methyl iodide.

The second substance, *iodoacetonylstrychnic acid*,

$$NH{:}C_{20}H_{22}O(CO_2H){:}NI\cdot CH_2\cdot COMe,$$

when dried in a vacuum loses half a molecule of water, forming an *anhydro-acid*, $(C_{24}H_{28}O_3N_2I)_2O$. It forms salts with salts of the heavy metals; with potassium dichromate a yellow, flocculent precipitate, $(C_{24}H_{29}O_4N_2)Cr_2O_7$, is obtained. The *picrate*, $C_{30}H_{31}O_{11}N_5$, is yellow. It reduces Fehling's solution, and forms a *phenylhydrazone*, m. p. 124°. With sodium nitrite in acid solution a crystalline precipitate of the nitrosoamine sulphate is formed.

With alkaline methyl-alcoholic methyl iodide, *iodoacetonyl*-N-*methylstrychnic acid*, $C_{25}H_{31}O_4N_2I$, is obtained; it crystallises in needles, m. p. 248°.

Analogous compounds could not be obtained from other alkaloids. Di-iodobrucine and acetone interact to give a *periodide*,

$$C_{23}H_{26}O_4N_2,HI,I_2,$$

crystallising in short, hard, brownish-red columns, m. p. 260°.

From di-iodocinchonine or di-iodoquinidine and acetone, the hydriodides of the bases were obtained. E. F. A.

Reduction Catalysts. V. Hydrogenation of Alkaloids. Aladar Skita and H. H. Franck (*Ber.*, 1911, **44**, 2862—2867).—Strychnine in dilute acetic acid containing a little 1% palladium chloride and 1% gum arabic is reduced in hydrogen under a pressure of 2 atmospheres at the ordinary temperature to *dihydrostrychnine*, $C_{21}H_{24}O_2N_2$, m. p. 209—210°, whilst brucine is converted into *dihydrobrucine*, $C_{23}H_{28}O_4N_2$, m. p. 115°, under similar conditions; under a pressure of 3 atmospheres at 70°, dihydrostrychnine is reduced further to Tafel's tetrahydrostrychnine.

In hydrochloric acid solution containing a little palladium chloride (or platinic chloride), morphine, codeine, quinine, and cinchonine are reduced by hydrogen to dihydromorphine (Oldenberg, this vol., i, 668), *dihydrocodeine*, $C_{18}H_{23}O_3N$, m. p. 65°, dihydroquinine, and dihydrocinchonine respectively, whilst piperine is converted into *tetrahydropiperine*, b. p. 261°/14 mm. These last reductions are not effected by the colloidal metal. C. S.

Strychnine Alkaloids. XII. Derivatives of Bis*apo*methylbrucine. HERMANN LEUCHS and RUDOLPH ANDERSON (*Ber.*, 1911, 44, 3040—3049. Compare this vol., i, 746).—The *nitrate*,

$$C_{21}H_{22}O_4N_2,HNO_3,1\tfrac{1}{2}H_2O,$$

hydrobromide, $C_{21}H_{22}O_4N_2,HBr,2H_2O$, *zincichloride*,

$$C_{21}H_{22}O_4N_2,H_2ZnCl_4,H_2O,$$

diacetyl derivative, $C_{25}H_{26}O_6N_2$, m. p. 232—233°, and the *methiodide*, m. p. 280° (decomp.), of bis*apo*methylbrucine are described. The action of concentrated nitric acid at −5° on bis*apo*methylbrucine yields *nitrobis*apo*methyldehydrobrucine nitrate*,

$$C_{21}H_{19}O_6N_3,HNO_3,3H_2O,$$

orange needles, which is converted by warm 10% nitric acid into cacotheline. The latter is obtained directly by warming bis*apo*methylbrucine hydrochloride with 10% nitric acid.

An attempt to regenerate brucine from bis*apo*methylbrucine by means of methyl iodide failed. However, with a large excess of methyl sulphate, bis*apo*methylbrucine hydrochloride in alkaline solution yields *brucine methosulphate*, $C_{23}H_{26}O_4N_2,Me_2SO_4,2\tfrac{1}{2}H_2O$, m. p. 268° (decomp.), which crystallises in three forms, has a very bitter taste, and responds to the red brucine reaction. This substance, which is identical with that obtained from methyl sulphate and brucine itself, is converted by warm aqueous sodium hydroxide into methylbrucine, the *acetyl* derivative of which has m. p. 157—158°, after strongly sintering at about 120° and resolidifying. When boiled with 10% nitric acid, methylbrucine yields *cacotheline methonitrate*, $C_{21}H_{21}O_7N_3,MeNO_3,2H_2O$, orange plates, which carbonises at about 280°. C. S.

Strychnine Alkaloids. XIII. Isolation of a Fourth Brucinesulphonic Acid. HERMANN LEUCHS and WALTER GEIGER (*Ber.*, 1911, 44, 3049—3051).—When brucine is sulphonated by manganese dioxide and sulphurous acid in the manner described previously (Abstr., 1908, i, 563; 1909, i, 120, 253, 602, 671), and the resulting sulphonic acids are extracted with water, a very small amount (3%) of a very sparingly soluble *brucinesulphonic acid*, $C_{23}H_{26}O_7N_2S,4H_2O$, is left undissolved. This acid crystallises in large, truncated prisms, has $[\alpha]_D^{20}$ −122·2° in N/10-alkali, and is soluble in 170 parts of boiling water. C. S.

Tetrahydropiperine and Tetrahydropiperic Acid. WALTHER BORSCHE (*Ber.*, 1911, 44, 2942—2945. Compare this vol., i, 880).—β-Styrylacrylic acid is readily reduced by palladium and hydrogen to δ-phenylvaleric acid, and the same method applied to piperine furnishes a quantitative yield of tetrahydropiperine, which on hydrolysis gives piperidine and tetrahydropiperic acid. The latter crystallises from dilute alcohol in colourless leaflets, m. p. 100—101° (compare Buri, Abstr., 1883, 485). The *methyl* ester, b. p. 193—195°, is a colourless, odourless oil. The *acid chloride* is a mobile oil, and on distillation decomposes, giving (1) a brown, resinous residue, which evolves hydrogen chloride, and (2) a viscid, colourless liquid, which deposits crystals. The *amide*, m. p. 110°, prepared from the chloride,

crystallises in glancing leaflets. The chloride on treatment with aluminium chloride in carbon disulphide gives *methylenedioxybenzosuberenone*, $\begin{matrix}CH_2\text{———}CO \\ | \qquad\qquad\quad \\ CH_2\cdot CH_2\cdot CH_2\end{matrix}\!\!>C_6H_2<\begin{matrix}O\\O\end{matrix}>CH_2$, as a nearly colourless oil, yielding a *semicarbazone*, m. p. 238—239° (decomp.), crystallising in small, colourless needles. T. A. H.

Synthesis of 2 : 4-Dimethyl-3-ethylpyrrole, a Contribution to the Question of the Constitution of Hæmopyrrole. LUDWIG KNORR and KURT HESS (*Ber.*, 1911, 44, 2758—2767).—According to Piloty (this vol., i, 92), hæmopyrrole is 2 : 4-dimethyl-3-ethylpyrrole, whilst phonopyrrole is 2 : 3-dimethyl-4-ethylpyrrole, but the synthesis of these substances has not yet been accomplished. The present authors have prepared 2 : 4-dimethyl-3-ethylpyrrole from 3-acetyl-2 : 4-dimethylpyrrole, obtained from the ethyl carboxylate produced by combination of nitrosoacetoacetic ester with acetylacetone. The synthetic product is similar to, but not identical with, hæmopyrrole, which must be 2 : 3-dimethyl-4-ethylpyrrole, therefore, in view of Piloty's work. The identity of 2 : 4-dimethyl-3-ethylpyrrole with phonopyrrole remains to be established, owing to the lack of crystalline derivatives of the latter substance. 2 : 3 : 5-Trimethylpyrrole (compare Ciamician and Dennstedt, *Ber.*, 1881, 14, 1340), 2 : 5-dimethyl-3-ethylpyrrole, and 2 : 5-dimethyl-3-propylpyrrole are also described.

The preparation of the pyrrole derivatives from the oximinoketones and acetoacetic ester was effected by the method formerly described (Knorr, Abstr., 1887, 275). The saponification of the carboxylic esters was carried out with 10% alcoholic sodium hydroxide containing a little water. On heating, the carboxylic acids lose carbon dioxide, the reaction being conducted in an atmosphere of nitrogen or hydrogen.

Ethyl 2 : 3 : 5-*trimethylpyrrole*-4-*carboxylate*, $C_{10}H_{15}O_2N$ (by reduction of methyl oximinoethyl ketone and acetoacetic ester), crystallises in small needles, m. p. 104—105°. The *acid*, $C_8H_{11}O_2N$, decomposes at 198°. 2 : 3 : 5-*Trimethylpyrrole*, $C_7H_{11}N$, has b. p. 180—181°/754 mm. (corr.).

Ethyl 2 : 5-*dimethyl*-3-*ethylpyrrole*-4-*carboxylate*, $C_{11}H_{17}O_2N$ (from methyl oximinopropyl ketone and acetoacetic ester), crystallises in small needles, m. p. 106—107°. The *acid*, $C_9H_{13}O_2N$, decomposes at about 200°. 2 : 5-*Dimethyl*-3-*ethylpyrrole*, $C_8H_{13}N$, has b. p. 187—188°/759 mm. (corr.), 93—94°/21 mm. It shows the pine splinter reaction, and gives a white precipitate with mercuric chloride, but differs from its isomerides in having an odour reminiscent of chloroform, and in being much less sensitive to oxygen.

Ethyl 2 : 5-*dimethyl*-3-*propylpyrrole*-4-*carboxylate*, $C_{12}H_{19}O_2N$ (from iso*nitrosobutyl methyl ketone*, which has m. p. 60°, and acetoacetic ester), forms prismatic crystals, m. p. 110°. The *acid*, $C_{10}H_{15}O_2N$, has m. p. about 210° (decomp.). 2 : 5-*Dimethyl*-3-*propylpyrrole*, $C_9H_{15}N$, has b. p. 206—207°/760 mm.

For the preparation of 2 : 4-dimethyl-3-ethylpyrrole another method had to be devised, advantage being taken of the fact (L. Wolff,

unpublished) that hydrazones can be reduced to hydrocarbons with sodium ethoxide. 3-*Acetyl*-2 : 4-*dimethylpyrrolehydrazone* (compare Knorr and Lange, Abstr., 1902, i, 821), $C_8H_{13}N_3$, forms rhombic crystals, m. p. 178—179°. When this substance is heated with an alcoholic solution of sodium ethoxide for fourteen hours at 150—160° in a sealed tube filled with nitrogen, 2 : 4-*dimethyl*-3-*ethylpyrrole* is produced, and is isolated by distillation in steam, saturation of the distillate with ammonium sulphate, and extraction with ether, care being taken to conduct all the operations in an atmosphere of hydrogen. The distillation of the substance is carried out as indicated by Piloty (*loc. cit.*) for hæmopyrrole. 2 : 4-Dimethyl-3-ethylpyrrole, $C_8H_{13}N$, has b. p. 96°/16 mm., 107°/27 mm., 118°/37 mm. It behaves like hæmopyrrole towards nitrous acid, yielding methylethylmaleinimideoxime, but is not fluorescent, and yields a *picrate* which forms compact crystals, m. p. 131—132° (hæmopyrrole picrate has m. p. 108·5°).

R. V. S.

Products from Pyrrole-2-carboxylic Acid. EMIL FISCHER and DONALD D. VAN SLYKE (*Ber.*, 1911, **44**, 3166—3171).—Pyrrole-2-carboxylic acid, in spite of the sensitiveness of the pyrrole ring to acids, is relatively easily converted into the chloride by phosphorus pentachloride. The chloride affords a convenient material for the preparation of the ester, amide, and anilide of the acid; it has also been coupled with glycine to form 2-pyrroylglycine,

$$CH{<}{\genfrac{}{}{0pt}{}{CH:C\cdot CO\cdot NH\cdot CH_2\cdot CO_2H}{CH\cdot NH}}.$$

Pyrrole-2-carboxylic acid shows a very marked red coloration in aqueous or alcoholic solution with ferric chloride, and resembles in this respect the phenolcarboxylic acids.

a-Pyrrolecarboxyl chloride, $C_4H_4N\cdot COCl$, crystallises in long, yellow needles, aggregated in bunches, m. p. about 90°. When carefully purified, it forms very long, colourless crystals, which sinter at 110°, and subsequently blacken without melting.

Pyrrole-2-*carbanilide*, prepared by interaction of pyrrolecarboxyl chloride and aniline in ethereal solution, forms colourless, long, and much intergrown prisms, m. p. 153—154° (corr.) after previous sintering.

a-Pyrroylglycine ethyl ester crystallises in six-sided platelets, m. p. 118° (corr.). *a-Pyrroylglycine* forms small, spindle-shaped crystals, m. p. 167° (corr.). It gives no coloration with ferric chloride.

E. F. A.

Action of Ammonia on Benzoyldehydracetic Acid. PAVEL IW. PETRENKO-KRITSCHENKO and JOH. SCHÖTTLE (*Ber.*, 1911, **44**, 2826—2830).—Feist's so-called 2 : 6-diphenyl-4-pyridone, obtained from benzoyldehydracetic acid and ammonia (Abstr., 1891, 458), is not identical with the author's compound of the same name (Abstr., 1909, i, 605), and is proved to be probably the *lactam*,

$$NH{<}{\genfrac{}{}{0pt}{}{CPh{=}CH}{CO\cdot CHBz}}{>}CO,$$

of benzoyldehydracetic acid by analysis, and by the fact that it is

converted by alcoholic potassium hydroxide into 2:6-*diphenyl*-4-*pyridone*-3-*carboxylic acid*, $NH<\begin{matrix}CPh{=\!=\!=}CH\\CPh{:}C(CO_2H)\end{matrix}>CO$, which yields 2:6-diphenyl-4-pyridone (m. p. 176—178°) at its m. p., 243—245°.

Feist's compound, which can also be converted into 2:6-diphenyl-4-pyridone hydrochloride by concentrated hydrochloric acid at 180°, is obtained from benzoyldehydracetic acid and alcoholic ammonia even at the ordinary temperature in two to three days (compare Feist, *loc. cit.*). C. S.

Toluoyl- and Xyloyl-picolinic Acids. OTTOKAR HALLA (*Monatsh.*, 1911, 32, 747—751).—Just (Abstr., 1898, i, 42) has obtained 3-*p*-toluoylpicolinic acid by the condensation of quinolinic anhydride with toluene in presence of aluminium chloride. Quinolinic acid affords an exception to Kirpal's rule that two isomeric ketonic acids are formed in this reaction, as he only obtained 3-benzoylpicolinic acid on condensing it with benzene.

It is now found that when condensed with toluene, 3-*p*-toluoylpicolinic acid, m. p. 169°, is the main product, but that traces of a compound, m. p. 150°, are also formed; this has not been investigated.

The 3-*p*-tolyl pyridyl ketone obtained by Just on heating 3-*p*-toluoylpicolinic acid at its melting point, has been synthesised from nicotinyl chloride and toluene; this establishes the formula of the 3-*p*-toluoylpicolinic acid, which has also been synthesised from quinolinic acid methyl ester chloride and toluene.

3-(m:4)-*Xyloylpicolinic acid*, prepared in a similar manner from *m*-xylene, has m. p. 142°. On heating, β-m:4-*xylyl pyridyl ketone* is obtained, identical with that prepared from nicotinyl chloride and xylene; it is a faintly yellow-coloured oil, b. p. 240°, and forms a *picrate*, crystallising in yellow plates, m. p. 134°. E. F. A.

Aldehydes of Oxindole, Indoxyl, and Hydroxythionaphthen. PAUL FRIEDLÄNDER and ST. KIELBASINSKI (*Ber.*, 1911, 44, 3098—3108).—Friedländer and Schwenk (Abstr., 1910, i, 592) have shown that indigotin is decomposed by potassium hydroxide at 150° into anthranilic acid and indoxylaldehyde. In a similar manner the isomeric oxindolealdehyde, $C_6H_4<\begin{matrix}C(CHO)\\NH\text{——}\end{matrix}>C{\cdot}OH$, is obtained from "thioindigoscarlet R," whilst the dye prepared by condensing hydroxythionaphthen with *N*-methylisatin yields a *N*-methyl derivative of oxindolealdehyde, $C_6H_4<\begin{matrix}C(CHO)\\NMe\text{——}\end{matrix}>C{\cdot}OH$. All three compounds show the normal aldehyde reactions.

Indoxylaldehyde, however, behaves abnormally towards mineral acids, which on moderate warming convert it into an intense violet dye; this dissolves in alkalis with a bluish-green coloration.

3′-Indoxyl-2-thionaphthen-2′-one (Abstr., 1908, i, 673) is decomposed by alkali to 3-hydroxythionaphthen-2-aldehyde,

$$C_6H_4<\begin{matrix}C(OH)\\S\text{——}\end{matrix}>C{\cdot}CHO;$$

this is converted quantitatively by dilute acids into a red dye dis-

solving in alkali with a bluish-violet coloration. This dye is also formed from equal molecules of hydroxythionaphthen and hydroxythionaphthenaldehyde, and has the constitution

$$C_6H_4<\begin{matrix}C(OH)\\S\end{matrix}>C\cdot CH:C<\begin{matrix}CO\\S\end{matrix}>C_6H_4.$$

The same dye is formed from hydroxythionaphthen under a variety of conditions; for example, by the action of air on the strongly alkaline solution, particularly in presence of formaldehyde or other aliphatic aldehyde. It is also formed on heating carboxyphenylsulphoxideacetic acid, $CO_2H\cdot C_6H_4\cdot SO\cdot CH_2\cdot CO_2H$, in anhydrous potassium sodium acetate at 160—170°.

It is probable that the dye formation from indoxylaldehyde is similar in character, and that it may be formulated as

$$C_6H_4<\begin{matrix}C(OH)\\NH\end{matrix}>C\cdot CH:C<\begin{matrix}CO\\NH\end{matrix}>C_6H_4.$$

Other analogous hydroxyaldehydes, for example, indandionealdehyde, $C_6H_4<\begin{matrix}C(OH)\\CO\end{matrix}>C\cdot CHO$, behave similarly towards acids.

The 3-aldehydes of oxindole and 2-hydroxythionaphthen are likewise sensitive towards mineral acids; the latter,

$$C_6H_4<\begin{matrix}C(CHO)\\S\end{matrix}>C\cdot OH,$$

is prepared by the action of potassium hydroxide on 2′-indoxyl-3-thionaphthen-2-one (*loc. cit.*).

Oxidole-3-aldehyde crystallises in faintly yellow-coloured needles, m. p. 213°; the aqueous solution is turned dark blue by ferric chloride. The *sodium* salt forms light grey crystals. The *phenylhydrazone* separates in stellar aggregates of pale yellow needles, m. p. 210°. The *aldazine* forms orange-yellow needles, m. p. 239°. The *oxime* forms corny crystals, m. p. 150°; its hydrochloride and sulphate crystallise well. The *anil* crystallises in yellow needles, m. p. 246° (decomp.). Analogous sparingly soluble anils are formed with *benzidine*, yellow needles, m. p. 300°, p-*toluidine*, greenish-yellow plates, m. p. 173°, m-*aminobenzoic acid*, yellow needles, m. p. above 290°, p-*phenylenediamine*, yellow plates, m. p. above 300°.

1-*Methyloxindole-3-aldehyde* crystallises in pale yellow needles, m. p. 186°; the *sodium* salt is sparingly soluble. The following derivatives are described: *phenylhydrazone*, broad, pale yellow needles, m. p. 193°; *oxime*, small, yellow, indefinitely formed needles, m. p. 111°; *aldazine*, orange-yellow needles, m. p. 211°; *anil*, pale yellow needles, m. p. 141°; *benzidine* derivative, greenish-yellow needles, m. p. 218°; p-*toluidine* derivative, well-formed, yellow needles, m. p. 150°; m-*aminobenzoic acid* derivative, yellow needles, m. p. 296°; p-*phenylenediamine* compound, orange-yellow needles, m. p. 210° (decomp.).

Indoxyl-2-aldehyde, m. p. 145°, forms a *phenylhydrazone*, crystallising in yellow needles, m. p. 116° (decomp.); the *aldazine* forms small, orange-red needles, decomp. above 150°; the *anil* gives orange-yellow needles, m. p. 195° (decomp.).

3-*Hydroxythionaphthen-2-aldehyde* crystallises in yellow needles, m. p. 107°, and gives a dark olive-green coloration with ferric chloride. The *phenylhydrazone* crystallises in broad, golden-yellow needles,

m. p. 137°. The *dye*, $C_{17}H_{10}O_2S_2$, obtained on warming with 5% sulphuric acid crystallises in large, red needles; the *sodium* salt forms lustrous, gold platelets. The corresponding *dye*, $C_{17}H_9O_2S_2Cl$, obtained on condensing hydroxythionaphthenaldehyde with 6-chlorohydroxythionaphthen, is very similar, crystallising in slender, red needles.

2-*Hydroxythionaphthen-3-aldehyde* crystallises in colourless needles, m. p. 126—127°; it gives a dark blue coloration with ferric chloride. The *aldazine* forms slender, yellow needles, m. p. 203°; with anthranilic acid a yellow, crystalline precipitate, m. p. 249°, of the *azomethine* is obtained. E. F. A.

Cyclic Ammonium Bases. HERMAN DECKER and ADOLF KAUFMANN (*J. pr. Chem.*, 1911, [ii], **84**, 425—448. Compare this vol., i, 807).—An aqueous solution of *iso*quinoline methiodide, when treated with potassium hydroxide and shaken with benzene, yields the corresponding carbinol base (1-hydroxy-2-methyldihydro*iso*quinoline). By shaking the benzene solution with water, the greater part of the carbinol base may be extracted in the form of the ammonium base (2-methyl*iso*quinolinium hydroxide), the amount of which may be determined by titration with hydrochloric acid. The dilute aqueous solutions thus obtained are strongly alkaline, precipitate metallic hydroxides, and show all the characteristic properties of aqueous solutions of aliphatic ammonium bases. In contrast to the carbinol base, which undergoes atmospheric oxidation very readily, the ammonium base is very stable, its aqueous solutions showing no change even on exposure to air for seventy-two hours. Dilute aqueous solutions of the ammonium base, when shaken with benzene, yield no appreciable amount of the carbinol base; on the addition of sodium hydroxide, however, considerable quantities of the carbinol base may be extracted.

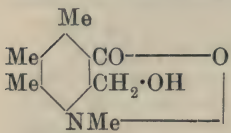
From these observations the conclusion is drawn that in aqueous solution there exists an equilibrium between the ammonium and carbinol bases: $C_6H_4{<}\begin{matrix}CH{:}CH \\ CH{:}NMe{\cdot}OH\end{matrix} \rightleftharpoons C_6H_4{<}\begin{matrix}CH{=\!=}CH \\ CH(OH){\cdot}NMe\end{matrix}$; in dilute solution the amount of the latter base is very small, but increases on the addition of an alkali hydroxide.

2-*Methyl*iso*quinolinium picrate*, $C_{16}H_{12}O_7N_4$, crystallises in long, slender, yellow needles, sintering at 183°, m. p. 187°.

Similar experiments were carried out with quinoline methiodide, but no evidence of the transformation of the carbinol base into the corresponding ammonium base was obtained.

[With MATEI SASSU and WASLAW WISLOKI.]—Addition of aqueous sodium hydroxide to pyridine methiodide yields a solution, which resembles in its behaviour that obtained from an aliphatic quaternary ammonium salt, and it has therefore been assumed (Hantzsch and Kalb, Abstr., 1900, i, 113) that the base is present in solution wholly in the ammonium form. The ready oxidation of such a solution to 1-methylpyridone (Decker, Abstr., 1893, i, 279) is, however, in contradiction to this view, but is readily explicable on the assumption that there exists in aqueous solution an equilibrium between the ammonium and carbinol bases, the amount of the latter being very small in com-

parison with that of the ammonium base. On oxidation, the carbinol base is continuously removed, and the equilibrium thereby displaced



until the whole of the ammonium base is converted into 1-methylpyridone.

Reasons are given in favour of the annexed formula for the compound obtained by Wolf (Abstr., 1902, i, 677) by the action of alkalis on trimethylquinolide methiodide.

1-Alkylpyridones are readily prepared by oxidising 1-alkylpyridinium halides with potassium ferricyanide in aqueous sodium hydroxide in the presence of benzene. The preparation of 1-methylpyridinium salts is best accomplished by treating the extremely hygroscopic *additive* compound of methyl sulphate and pyridine with the acid corresponding with the salt required; the picrate, $C_{12}H_{10}O_7N_4$, is thus obtained anhydrous in needles, m. p. 113—114°, or rhombohedra, m. p. 109—110°.

1-*Propylpyridinium bromide* (*pyridine propylbromide*), prepared from pyridine and propyl bromide, yields a *cadmibromide*, $C_{16}H_{24}N_2Br_4Cd$, crystallising in white needles, m. p. 117—118°; the *chloride*, *mercurichloride*, m. p. 82°, and *platinichloride*, orange-red crystals, m. p. 196°, are also described.

1-*Propyl*-2-*pyridone*, $C_8H_{11}ON$, is a light yellow liquid, b. p. 263—264°/730 mm., having a repulsive odour of fungi.

1-iso*Butylpyridinium iodide* forms very hygroscopic, light yellow crystals; the *picrate*, leaflets, m. p. 114°; the *platinichloride*, yellow leaflets, m. p. 220° (decomp.). 1-iso*Butyl*-2-*pyridone*, $C_9H_{13}ON$, is a yellow oil, b. p. 264—265°/725 mm.

1-iso*Amylpyridinium iodide* forms hygroscopic crystals; the *picrate*, yellow needles, m. p. 145°, and the *platinichloride*, yellow leaflets, which decompose at 200°, were also prepared. 1-iso*Amyl*-2-*pyridone* has b. p. 283—284°/730 mm.

3-*Bromopyridine methiodide* crystallises in hygroscopic, yellow needles, m. p. 146°, and is oxidised by potassium ferricyanide to 3-*bromo*-1-*methyl*-2-*pyridone*, which forms a brown oil, and on treatment with bromine in glacial acetic acid solution yields 3 : 5-*dibromo*-1-*methyl*-2-*pyridone*; the latter compound, which crystallises in white needles, m. p. 176°, has also been prepared (1) by the oxidation of the *additive* compound of methyl sulphate and 3 : 5-dibromopyridine; (2) by brominating 1-methylpyridone. 3 : 5-*Dibromopyridine methiodide*, obtained by the action of potassium iodide on the above-mentioned additive compound, resembles *iso*quinoline methiodide in its behaviour towards alkalis.

[With S. Pfeifer, N. Prohatzka, and A. Albertini.]—The entrance of substituents into quaternary quinoline salts considerably modifies the behaviour of the latter towards alkalis; whilst 6-aminoquinoline methiodide on treatment with aqueous sodium hydroxide undergoes no change, the dinitro- and bromonitro-derivatives are converted into the corresponding carbinol bases by dilute sodium hydrogen carbonate. It thus appears that positive substituents prevent the transformation of ammonium bases into carbinol bases, whilst

with negative substituents the transformation takes place with extraordinary ease.

6-*Diacetylaminoquinoline*, prepared by heating 6-aminoquinoline with acetic anhydride in benzene solution, crystallises in long, slender, white needles, m. p. 75°; the product, obtained by the interaction of the *methiodide* and silver chloride, yields either 6-*diacetylaminoquinoline methochloride* or 6-*acetylaminoquinoline methochloride*, accordingly as it is crystallised from alcohol or water.

6-Acetylamino-1-methylquinolone, prepared by oxidising 6-*acetylaminoquinoline methiodide*, crystallises in needles, m. p. 278° (compare Decker and Engler, Abstr., 1903, i, 518).

6-*Aminoquinoline methochloride*, obtained by heating the acetyl (or diacetyl) derivative with hydrochloric acid, crystallises in citron-yellow needles, m. p. 242—243°; it separates from water in efflorescent crystals containing one molecule of the solvent; the methiodide forms reddish-brown needles, m. p. 199° (compare Claus and Schnell, Abstr., 1896, i, 319). When treated with 35% aqueous sodium hydroxide, 6-aminoquinoline methiodide yields a *substance*,

$$C_{20}H_{29}O_4N_2I,$$

crystallising in microscopic, red needles, m. p. 166°, which have a vivid green, metallic lustre, and yield solutions having a yellow fluorescence.

6 : 8-*Dinitro*-2-iso*butyloxy*-1-*methyldihydroquinoline*,

$$C_{14}H_{17}O_5N_3,$$

has m. p. 87°; the methyl and ethyl ethers (Kaufmann and Strübin, this vol., i, 322) are also described.

6-Bromo-8-nitroquinoline, which has m. p. 170—177° (compare Claus and Hartmann, Abstr., 1896, i, 391), on successive treatment with methyl sulphate and potassium iodide yields the *methiodide*, $C_{10}H_8O_2N_2BrI$, which crystallises in dark reddish-brown needles, decomposing at 185—186°. With dilute aqueous ammonia the methiodide yields 6-*bromo*-8-*nitro*-2-*hydroxy*-1-*methyldihydroquinoline*, which has m. p. 173—175°, and forms a *methyl ether*, m. p. 121—122°; the *ethyl ether* crystallises in prisms, m. p. 111°.

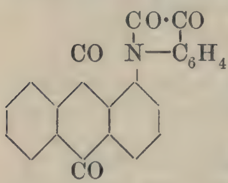
3 Bromo-8-nitro-2-hydroxy-1-methyldihydroquinoline (Decker, Abstr., 1905, i, 374) is obtained in quantitative yield by the action of very dilute aqueous ammonia on the methiodide; the *ethyl ether*, large, light brown, prismatic crystals, has m. p. 90—91°. F. B.

Preparation of Halogen-substituted Indophenol Derivatives from Carbazoles and *p*-Nitrosophenols. LEOPOLD CASSELLA & Co. (D.R.-P. 235836).—When *p*-nitrosophenol or its halogen derivatives are condensed in concentrated sulphuric acid solution with *N*-alkyl or halogenated carbazoles, indophenol derivatives of tinctorial value are produced.

The *products* from monochlorocarbazole and *p*-nitrosophenol, from carbazole and *N*-ethylcarbazole with *o*-chloronitrosophenol respectively, and from carbazole with 2 : 6-dibromonitrosophenol were prepared. They are dark blue or green substances, insoluble in water, but soluble in concentrated sulphuric acid with a blue

coloration, decompose above 250° without fusion, and yield colourless leuco-compounds. F. M. G. M.

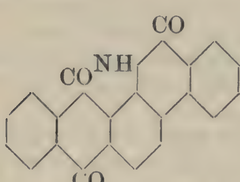
[Preparation of Anthraquinone Derivatives.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 236407).—When α-chloroanthraquinone is boiled with isatin (in nitrobenzene solution) in the presence of cuprous chloride and copper acetate and the mixture subsequently acidified, it yields the *compound* (annexed formula) as a bluish-red, crystalline powder. The *products* from 1 : 5-dichloroanthraquinone and isatin (1 mol.), a violet powder, and the same with 2 mols. of isatin were also prepared, whilst 4-bromo-1-methylaminoanthraquinone under similar conditions yielded a greenish-black powder. F. M. G. M



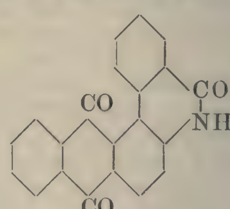
Preparation of Phenanthridone Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 236857).—When halogen-*o*-benzoylaminoanthraquinones (or their derivatives) are boiled with or without copper powder in naphthalene solution with anhydrous sodium carbonate (or acetate), condensation occurs, yielding phenanthridone derivatives.

The *compound* (I), $C_{21}H_{11}O_3N$, prepared from 2-bromo-1-benzoylaminoanthraquinone (without the addition of copper powder), crystallises from dichlorobenzene, and has m. p. 266—267°.

The *compound* (II), m. p. 274—275°, was obtained from 1-chloro-2-benzoylaminoanthraquinone in nitrobenzene solution without copper powder. The *products* from 2 : 3-dichloro-1 : 4-dibenzoylaminoanthra-



(I.)



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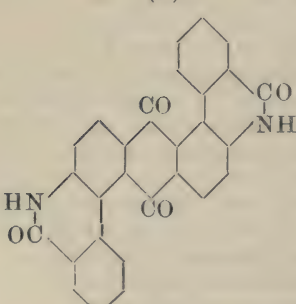
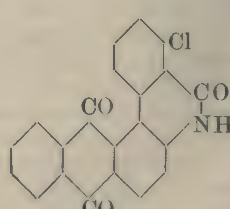


(III.)



(IV.)

quinone and from 3-halogen-2-benzoylaminoanthraquinone do not fuse below 325°.

The *product* (III), $C_{28}H_{14}O_4N_2$, prepared from 1 : 5-dichloro-2 : 6-dibenzoylaminoanthraquinone in the presence of copper, does not melt at 320°.

The *compound* (IV), $C_{21}H_{10}O_3NCl$, m. p. 278—280°, was obtained from 1-chloro-*o*-chlorobenzoylaminoanthraquinone (prepared from *o*-chlorobenzoyl chloride and 1-chloro-2-aminoanthraquinone).

F. M. G. M.

[Preparation of Carbamide Derivatives.] CARL JÄGER (D.R.-P. 236594).—When an aromatic *m*-diamino-sulphonic acid (1 mol.) reacts with an aminonaphtholsulphonic acid (2 mols.) and carbonyl chloride (2 mols.) in dilute aqueous sodium carbonate solution, derivatives of carbamide are obtained. The *substance*,

$$SO_3H\cdot C_6H_2Me[NH\cdot CO\cdot NH\cdot C_{10}H_5(OH)\cdot SO_3H]_2,$$

is prepared in this manner from 2 : 6-tolylenediamine-4-sulphonic acid, 6-amino-α-naphthol-3-sulphonic acid, and carbonyl chloride. These compounds when combined with 2 mols. of a diazonium compound yield orange to bluish-red direct cotton dyes. F. M. G. M.

Catalytic Decomposition of Alkylidenehydrazines. II. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 951—962).—With a view to generalising the method of obtaining hydrocarbons previously described (this vol., i, 679), the author has studied the decomposition, in presence of potassium hydroxide, of the hydrazones of dihydrocarvone, carvenone, citronellaldehyde, and citral.

Under these conditions, dihydrocarvonehydrazone yields $\Delta^{8(9)}$-*p*-menthene (compare Perkin and Pickles, Trans., 1905, **87**, 639). The action of hydrobromic acid on this hydrocarbon gives the bromo-derivative, $C_{10}H_{19}Br$, which yields *i*-$\Delta^{4(8)}$-menthene (compare Wallach, Abstr., 1906, i, 682) when distilled with aniline.

Carvenonehydrazone, when distilled in presence of fused potassium hydroxide, yields Δ^3-menthene.

Citronellaldehydehydrazone yields the *hydrocarbon*,

$$CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_3,$$

b. p. 164·5°/756 mm., D_0^{20} 0·7533, n_D 1·4304, $[\alpha]_D$ + 9·28°. Oxidation of this hydrocarbon with permanganate yields acetone, active amylacetic acid (compare Welt, Abstr., 1895, i, 203), and, as an intermediate product, the *keto-alcohol*,

$$OH\cdot CMe_2\cdot CO\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2Me,$$

b. p. 218°/755 mm., D_0^{20} 0·9069, n_D 1·4363, which reduces ammoniacal silver solution in presence of alkali, and forms a *semicarbazone*, m. p. 125—126°, $[\alpha]_D$ + 1·78° to + 2·20°.

The hydrocarbon, b. p. 164·5°, obtained from citronellaldehyde-hydrazone, gives with hydrobromic acid the *bromo*-derivative,

$$C_{10}H_{21}Br,$$

D_0^{20} 1·0772, n_D 1·4578, which gives a hydrocarbon, $C_{10}H_{20}$, with almost the same physical constants as the original one when distilled with aniline, with the exception of its specific rotation, which is $[\alpha]_D$ + 4·39°.

Reduction of the hydrocarbon, b. p. 164·5°, by means of hydriodic acid in a sealed tube yields $\beta\zeta$-dimethyloctane,

$$CHMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHMeEt\ (?),$$

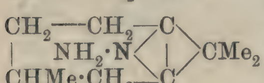
b. p. 159—159·5°/742 mm., D_4^{20} 0·7313, n_D 1·4110, $[\alpha]_D$ +1·75° (compare Markownikoff and Reformatsky, Abstr., 1893, i, 662; Skita and Ritter, *Ber.*, 1911, **44**, 668; this vol., i, 272).

Citralhydrazone, when distilled with solid potassium hydroxide yields an inactive *hydrocarbon*, $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe$, b. p. 164—165°/755 mm., D_0^{20} 0·7674, n_D 1·4443, which is isomeric with the dihydromyrcene, b. p. 171·5—173·5°, obtained by Semmler (Abstr., 1901, i, 732) by the reduction of myrcene. T. H. P.

Decomposition of Alkylidenehydrazines. Conversion of Pulegone [Tanacetone] into a Bicyclic Hydrocarbon, $C_{10}H_{18}$. NICOLAI M. KIJNER and A. ZAVADOVSKY (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1132—1148. Compare this vol., i, 679).—The action of hydrazine hydrate on tanacetone would be expected to give an alkylidenehydrazine of the structure

$$CHMe{<}{\begin{matrix}CH_2\text{———}CH_2\\ CH_2\cdot C({:}N\cdot NH_2)\end{matrix}}{>}C{:}CMe_2,$$

this yielding, on decomposition, $\Delta^{4(8)}$-menthene (compare Wallach, Abstr., 1908, i, 402). It is found, however, that pulegohydrazine is not hydrolysed by mineral acids, with which it forms stable salts, and that, on decomposition, it gives a dicyclic hydrocarbon, *carane*, $\begin{matrix}CH_2\text{—}CH_2\text{—}CH\\ |\qquad\qquad |\\ CHMe\cdot CH_2\cdot CH\end{matrix}{>}CMe_2$, corresponding with carone. The action of



hydrazine hydrate on pulegone is hence accompanied by isomerisation, pulegohydrazine having the annexed constitution.

Pulegohydrazine, $C_{10}H_{18}N_2$, is an almost colourless liquid, b. p. 131—132°/23 mm., 143—144°/35 mm., D_0^{20} 0·9602, $[\alpha]_D$ − 5·55°, n_D 1·4943. The *thiosemicarbazone*,

$$NHPh\cdot CS\cdot NH\cdot N{:}C_{10}H_{16},$$

forms thin, rhombic plates, m. p. 176°, $[\alpha]_D$ − 114·33°. The hydrazine undergoes oxidation in the air, yielding pulegone, and an oily product which was not investigated.

Carane, $C_{10}H_{18}$, obtained by the slow distillation of pulegohydrazine with potassium hydroxide, has b. p. 169·5°/759 mm., D_0^{20} 0·8404—0·8411, n_D 1·4561—1·4576, exaltation of molecular refraction 0·72—0·85, $[\alpha]_D$ + 56·89° to 57·64°. Carane is quite saturated in character, and, owing to the presence of the trimethylene ring (indicated by the optical exaltation) readily combines with 1 mol. of bromine or halogen hydroacid. The *bromo*-derivative, $CH_2{<}{\begin{matrix}CHMe\cdot CH_2\\ CH_2\text{——}CH_2\end{matrix}}{>}CH\cdot CMe_2Br$, obtained by the action of hydrobromic acid, has b. p. 123—124°/29 mm. (slightly decomp.), D_4^{20} 1·1811, D_0^{20} 1·1691, n_D 1·4893—1·4914, $[\alpha]_D$ + 5·37° to 5·42°, and loses hydrogen bromide in two different ways: (1) with alcoholic potassium hydroxide it gives $\Delta^{3(8)}$-*m*-menthene (compare Wallach, *loc. cit.*), which yields β-methyladipic acid when oxidised with excess of permanganate; (2) with aniline the principal

product is $\Delta^{8(9)}$-m-*menthene*, $CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2\text{---}CH_2\end{matrix}>CH\cdot CMe\colon CH_2$, which is, however, mixed with $\Delta^{3(8)}$-*m*-menthene.

When $\Delta^{8(9)}$-*m*-menthene is treated with hydriodic acid and the iodide heated with aqueous-alcoholic potassium hydroxide, $\Delta^{3(8)}$-*m*-menthene is obtained.

Reduction of carane or $\Delta^{8(9)}$-*m*-menthene yields *m*-menthane.

Combination of carane with bromine (1 mol.) and distillation of the bromide thus obtained with quinoline gives lævorotatory menthadiene, which, after prolonged boiling with sodium, becomes inactive, and has b. p. 182—185°/749 mm., D_4^{20} 0·8544, n_D 1·4916; this hydrocarbon in acetic anhydride solution gives an intense blue coloration with sulphuric acid. Such a coloration is given by $\Delta^{2:8(9)}$-*m*-menthadiene (compare Haworth, Perkin, and Wallach, Trans., 1911, 99, 118), but this could only be derived from carane as a result of isomerisation of the bromide previous to the removal of hydrogen bromide (see also Perkin, Trans., 1910, 97, 2154). T. H. P.

Influence of Auxochromes on Phototropy. Maurice Padoa and L. Santi (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 196—200. Compare this vol., i, 693).—On comparing the phototropic substances previously obtained, it appears that the aldehydrazones which contain auxochrome groups are generally more phototropic than those which do not contain any, and this is even more noticeable in the case of the osazones of diketones. The position of the auxochrome appears to have some influence. In the present paper eight anishydrazones (*p*-methoxyphenylhydrazones) are described, which have been prepared for comparison with the corresponding phenylhydrazones.

p-Methoxyphenylhydrazine (compare Altschul, Abstr., 1892, 1080) is best obtained by diazotising *p*-anisidine and reducing the diazonium compounds with stannous chloride. It has m. p. 66° (Altschul, 65°).

*Benzaldehyde-*p*-methoxyphenylhydrazone*, $OMe\cdot C_6H_4\cdot NH\cdot N\colon CHPh$, crystallises in pale yellow needles, m. p. 123°, and is phototropic.

*Anisaldehyde-*p*-methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot OMe,$$

forms lustrous, yellow scales, m. p. 126°, and is not phototropic.

*Cinnamaldehyde-*p*-methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot CH\colon CHPh,$$

crystallises in rosettes of short, thick needles, m. p. 126·5°, and is phototropic.

*Cuminaldehyde-*p*-methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot CHMe_2,$$

forms long, pale yellow needles, m. p. 99°. It is phototropic.

*Piperonaldehyde-*p*-methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot C_6H_3\colon O_2\colon CH_2,$$

crystallises in yellowish-green, lustrous needles, m. p. 134—135°, and is phototropic.

p-*Tolualdehyde-*p*-methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot C_6H_4Me,$$

forms lustrous, yellow scales, m. p. 131°, and is not phototropic.

*Vanillin-*p*-methoxyphenylhydrazone,*

$OMe\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot C_6H_3(OH)\cdot OMe$,

crystallises in minute, pale yellow prisms, m. p. 125—126°, and is phototropic.

*Salicylaldehyde-*p*-methoxyphenylhydrazone,*

$OMe\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot OH$,

forms yellowish-green needles, m. p. 132°, and is not phototropic.

R. V. S.

Phototropy of the Hydrazones of Furfuraldehyde. L. SANTI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 228—230. Compare Padoa and Graziana, Abstr., 1910, i, 509, 778).—Furfuraldehyde-phenylhydrazone is not phototropic.

Furfuraldehyde-α-naphthylhydrazone, $C_4H_3O\cdot CH\colon N\cdot NH\cdot C_{10}H_7$, forms small, canary-yellow prisms, m. p. 110·5°, and is not phototropic.

Furfuraldehyde-β-naphthylhydrazone crystallises in pale yellow needles, m. p. 137°, and is phototropic.

*Furfuraldehyde-*p*-tolylhydrazone*, $C_4H_3O\cdot CH\colon N\cdot NH\cdot C_6H_4Me$, is a pale yellow, crystalline powder, which is weakly phototropic.

R. V. S.

Action of Aldehydes on Pyrrole Derivatives. U. COLACCHI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 312—317).—Pyrrole derivatives which have only one free methine hydrogen, and have a negative substituent, react with aliphatic aldehydes when warmed with them in the presence of a little zinc chloride. The condensations with formaldehyde are best effected in the presence of hydrochloric acid.

Bis-5-acetyl-2 : 4-dimethylpyrrylmethane, $CH_2(C_4NHMe_2Ac)_2$, forms yellow scales or needles, m. p. 272°.

Bis-3-acetyl-2 : 4-dimethylpyrrylmethane, $CH_2(C_4NHMe_2Ac)_2$, is a yellow, crystalline powder, m. p. 268°.

Bis-5-benzoyl-2 : 4-dimethylpyrrylmethane, $CH_2(C_4NHMe_2Bz)_2$, crystallises in small, colourless needles, m. p. 257—258°.

αα-Bis-5-acetyl-2 : 4-dimethylpyrrylethane $CHMe(C_4NHMe_2Ac)_2$, forms yellow needles, m. p. 253°.

αα-Bis-3-acetyl-2 : 4-dimethylpyrrylethane, $CHMe(C_4NHMe_2Ac)_2$, crystallises in pale, rose-coloured scales, m. p. 254°.

αα-Bis-5-benzoyl-2 : 4-dimethylpyrrylethane, $CHMe(C_4NHMe_2Bz)_2$, forms very small prisms, m. p. 244—245°.

αα-Bis-5-benzoyl-2 : 4-dimethylpyrrylbutane, $CHPr(C_4NHMe_2Bz)_2$, crystallises in small, yellow prisms, m. p. 217—218°.

*αα-Bis-5-benzoyl-2 : 4-dimethylpyrryl*iso*butane*,

$CHMe_2\cdot CH(C_4NHMe_2Bz)_2$,

is a yellow, flocculent substance, which on heating becomes soft at 80°, spongy at 100°, and melts at 180°.

αα-Bis-5-benzoyl-2 : 4-dimethylpyrrylheptane,

$C_6H_{13}\cdot CH(C_4NHMe_2Bz)_2$,

forms a yellow, crystalline powder, m. p. 178—179°. R. V. S.

Preparation of Halogenated Derivatives of Indigotin. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 235631. Compare this vol., i, 925).—The preparation of tetrahalogenated indigotins has

previously been recorded; penta- and hexa-halogenated derivatives have now been prepared.

Dichlorotetrabromoindigotin is obtained when 4 : 4′-dichloroindigotin, dissolved in nitrobenzene (or acetic acid), is slowly treated with bromine and the mixture subsequently boiled until the evolution of hydrogen bromide ceases.

Pentachloroindigotin is prepared by the further chlorination of 4 : 4′-dichloroindigotin at 25—30° in acetic acid solution. The leuco-derivatives and intermediate halogenated acetylindigotins are also mentioned and their tinctorial properties described. F. M. G. M.

Hydantoins. VI. Action of Acylthioncarbamates, Acylthiocarbamates, Acyldithiocarbamates, and Acylimidodithiocarbonates on α-Amino-acids. 2-Thiolhydantoin. HENRY L. WHEELER, BEN H. NICOLET, and TREAT B. JOHNSON (*Amer. Chem. J.*, 1911, 46, 456—474).—This work was undertaken for the purpose of synthesising some *N*-acyl derivatives of hydantoic and thiohydantoic acids and of investigating their behaviour on hydrolysis and their reactivity towards aldehydes.

Benzoyl-ψ-ethylhydantoic acid, $NBz\colon C(OEt)\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 161°, obtained by the action of aminoacetic acid on ethyl benzoylthioncarbamate in presence of potassium hydroxide, crystallises in needles; its *ethyl* ester has m. p. 79—80°. *Ethyl benzoyl-ψ-methylhydantoate*, $NBz\colon C(OMe)\cdot NH\cdot CH_2\cdot CO_2Et$, m. p. 103°, is obtained by the interaction of ethyl aminoacetate and methyl benzoylthioncarbamate. When benzoyl-ψ-ethylhydantoic acid or ethyl benzoyl-ψ-methylhydantoate is hydrolysed with hydrochloric acid, *benzoylhydantoic acid*, $NHBz\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 253—254° (decomp.), is produced, which crystallises in plates, and is decomposed by hydrochloric acid into benzoic acid and hydantoin. An attempt to condense benzoylhydantoic acid with benzaldehyde was not successful.

Thiobenzoylhydantoic acid, $NHBz\cdot CS\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 202°, prepared by heating a mixture of aminoacetic acid, potassium hydroxide, and ethyl benzoyldithiocarbamate, crystallises in plates or needles; its *ethyl* ester has m. p. 128—129°. When either thiobenzoylhydantoic acid or thioacetylhydantoic acid is heated with concentrated hydrochloric acid, 2-*thiohydantoin*, $CH_2<\begin{matrix}CO-NH\\ NH\cdot CS\end{matrix}$, m. p. 227°, is produced, which forms yellow prisms. Benzoylthiohydantoic acid condenses with benzaldehyde to form 2-*thio*-1-*benzoyl*-4-*benzylidenehydantoin*, $CHPh\colon C<\begin{matrix}CO-NBz\\ NH\cdot CS\end{matrix}$, m. p. 181°, which crystallises in rectangular plates, and is decomposed by potassium hydroxide solution with production of 2-thio-4-benzylidenehydantoin, m. p. 258°, which can also be obtained by the condensation of thiohydantoin with benzaldehyde. Ruhemann and Stapleton (Trans., 1900, 77, 246) have stated that this compound has m. p. 280° (decomp.) when heated slowly and m. p. 300° (decomp.) when heated rapidly, but the authors found the m. p. 258° under all conditions.

Thiobenzoyl-ψ-ethylhydantoic acid, $NBz\colon C(SEt)\cdot NH\cdot CH_2\cdot CO_2H$, m. p.

198°, prepared from aminoacetic acid and ethyl benzoyliminodithiocarbonate, forms clusters of needles; its *ethyl* ester has m. p. 77—78°.

Thioacetylhydantoic acid, $NHAc\cdot CS\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 205° (decomp.), from aminoacetic acid and ethyl acetyldithiocarbamate, crystallises in slender needles; its *potassium* salt has m. p. 225—227° (decomp.), and its *ethyl* ester, m. p. 104—105°. The acid condenses with benzaldehyde to form 2-*thio*-1-*acetyl*-4-*benzylidenehydantoin*, $CHPh:C<\begin{matrix}CO-NAc\\ NH\cdot CS\end{matrix}$, m. p. 231°, which crystallises in light yellow prisms.

Thio-1-*acetyl*-4-*methylhydantoic acid*, $NHAc\cdot CS\cdot NH\cdot CHMe\cdot CO_2H$, m. p. 171°, from alanine and ethyl acetyldithiocarbamate, crystallises in prisms, and is converted by concentrated hydrochloric acid into 2-*thio*-4-*methylhydantoin*, $CHMe<\begin{matrix}CO-NH\\ NH\cdot CS\end{matrix}$, m. p. 158—159°, which forms flat prisms.

E. G.

Preparation of 5:5-Dialkylthiobarbituric Acids. EMANUEL MERCK (D.R.-P. 235801. Compare this vol., i, 683).—The preparation of 5:5-dialkylthiobarbituric acids by the employment of metallic alkyloxides has previously been described; it is found that these can be replaced by the free alkali metal (or its amide), and the preparation of diethylthiobarbituric acid (m. p. 180°) from diethylmalonic ester, thiocarbamide, and sodamide (or metallic sodium) is now demonstrated.

F. M. G. M.

Constitution of the Nitro-2:5-dimethylbenziminazole Obtained by Nitration. DAVID MARON and D. SALZBERG (*Ber.*, 1911, **44**, 2999—3005).—The proof that the nitro-group in the nitro-compound, m. p. 200—201°, obtained by the nitration of 2:5-dimethylbenziminazole (Niementowsky, Abstr., 1886, 719), occupies position 6 is as follows. By reduction with iron and 50% acetic acid, the nitro-compound yields an *amine*, m. p. 85°, the *acetyl* derivative of which has m. p. 263—264°. By nitration, diacetyl-*m*-tolylenediamine yields a nitro-compound, which can be reduced to an *amine*, m. p. 252—253°, which forms an azoimide with nitrous acid (therefore the amino-group is ortho to an NHAc group), and yields the preceding acetylaminodimethylbenziminazole, m. p. 263—264°, by heating at 250°. Finally, the nitration of diacetyl-3:4-tolylenediamine yields a nitro-compound, the reduction of which yields an *amine*, m. p. 238°, the *acetyl* derivative of which, m. p. 273—274°, is identical with that obtained by the acetylation of the preceding amine, m. p. 252—253°. Consequently, this acetylated triamino-derivative must be triacetyl-3:4:6-triaminotoluene; the amine m. p. 238° is 6-aminodiacetyl-3:4-tolylenediamine, the amine m. p. 252—253° is 3-aminodiacetyl-4:6-tolylenediamine, and the nitrated dimethylbenziminazole is 6-nitro-2:5-dimethylbenziminazole.

C. S.

Researches on Azinetriphenylpyrrole. FRANCESCO ANGELICO (*Gazzetta*, 1911, **41**, ii, 378—381).—By the action of ammonium sulphide on the diketone, $\begin{matrix}CH:CH\cdot C{-}{-}N:N\\ |\qquad\quad \| \qquad |\\ CH:CH\cdot C\cdot CBz:CBz\end{matrix}$ (compare Abstr., 1909,

i, 122), the author obtained (Abstr., 1910, i, 444) the corresponding *dithioketone*, m. p. 206°, and he has now isolated from the product of the same reaction, a thiophen *compound*, $C_{22}H_{14}N_2S$, which forms large, yellow needles, m. p. 151°. When treated with nitric acid this substance regenerates the ketone of m. p. 163°.

The structure of the dithioketone follows from the fact that both it and the diketone yield, when treated with hydroxylamine, the same products, namely: (1) a red pyrrole derivative; (2) a substance, probably a mixture of mono- and di-oximes; (3) a *substance*, $C_{44}H_{27}O_3N_9$, which crystallises in golden-yellow needles, m. p. 205—206°.

R. V. S.

5-Aminophenazoxonium Salts. FRIEDRICH KEHRMANN and L. LOWRY (*Ber.*, 1911, **44**, 3006—3011).—5-Aminophenazoxonium and 5-aminophenazthionium salts cannot be prepared in a similar manner to 5-aminophenylphenazonium salts (Kehrmann and Masslenikoff, this vol., i, 927). However, by the reduction of Ullmann and Kuhn's 5-nitrophenoxazine (Abstr., 1909, i, 473) by stannous chloride and concentrated hydrochloric acid, *5-aminophenoxazine hydrochloride*, $C_6H_4{<}{}^{NH}_{O}{>}C_6H_3{\cdot}NH_2,HCl$, is obtained, which is oxidised by cold concentrated ferric chloride to *5-aminophenazoxonium chloride*, $C_6H_4{<}{}^{-N-}_{OCl}{\geqslant}C_6H_3{\cdot}NH_2$, greenish-black crystals; the corresponding *bromide*, *iodide*, *nitrate*, and *platinichloride* are described.

When acetylated by sodium acetate, acetic anhydride, and a trace of zinc dust, 5-aminophenoxazine hydrochloride yields *5-acetylaminophenoxazine*, m. p. 197° (decomp.), colourless needles, which is oxidised by ferric chloride to a mixture of two substances, m. p. about 215° (decomp.), which are probably isomeric 5-acetylaminophenazoxones.

3 : 5-Diaminophenazoxonium chloride reacts with acetic anhydride and zinc chloride to form a blackish-red, crystalline *zincichloride*, from which *3-amino-5-acetylaminophenazoxonium chloride*,

$$C_6H_4{<}{}^{-N-}_{OCl}{\geqslant}C_6H_2(NH_2){\cdot}NHAc,H_2O,$$

is obtained in dark red prisms with a green lustre. The *platinichloride* is a brownish-red, crystalline powder, whilst the *base* itself, m. p. 185—190° (decomp.), crystallises in citron-yellow needles.

C. S.

Mutual Replacement of Azines and Semicarbazones. GUSTAV KNÖPFER (*Monatsh.*, 1911, **32**, 753—772).—It has been shown previously that the azine residue is readily replaced by phenylhydrazine, and this in turn by semicarbazide (Knöpfer, Abstr., 1909, i, 188; 1910, i, 432). It is now found that azines are very easily converted into semicarbazones, but that in most instances the reverse change does not take place. When aldehydes or ketones are treated with a molecular mixture of semicarbazide and hydrazine, the semicarbazone is, as a rule, the sole product.

The conversion into azine was observed in the case of the semicarbazones of salicylaldehyde, *p*-hydroxybenzaldehyde, *p*-nitrobenz-

aldehyde, resorcylaldehyde, protocatechualdehyde, *p*-dimethylamino-benzaldehyde, and acetone.

The *azine* of phenyl ethyl ketone forms yellow needles, m. p. 79—80°. The semicarbazone forms colourless crystals, m. p. 179—180°.

Distyryl ketone-semicarbazone forms colourless, soluble needles, m. p. 187—190°; *a-dichloroacetonesemicarbazone* has m. p. 163°, yielding a compound, m. p. 254°, which proved to be methylglyoxaldisemicarbazone.

Chloralhydrazide, $CCl_3\cdot CH(OH)\cdot NH\cdot NH_2$, forms large, colourless crystals, m. p. 85° (decomp.). The hydrazide is readily replaced by semicarbazide, forming chloral semicarbazide, m. p. 90°, but the reverse change does not take place.

The only substances to give both semicarbazone and azine on treatment with an equimolecular mixture of the two bases are *p*-nitrobenzaldehyde and *p*-dimethylaminobenzaldehyde. E. F. A.

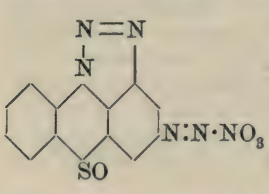
3 : 5 - Diaminophenazthionium Derivatives. FRIEDRICH KEHRMANN and J. STEINBERG (*Ber.*, 1911, **44**, 3011—3017).—The course of the reaction between picryl chloride and *o*-aminophenyl mercaptan proceeds, as stated by Kehrmann and Schild (Abstr., 1900, i, 61), not as by Mitsugi, Beyschlag, and Möhlau (Abstr., 1910, i, 337), the proof being as follows. A hot alcoholic solution of picryl chloride (2 mols.) condenses normally with *oo'*-diaminodiphenyl disulphide hydrochloride in the presence of sodium acetate, yielding oo'-*dipicryldiaminodiphenyl disulphide*, $[C_6H_2(NO_2)_3\cdot NH\cdot C_6H_4]_2S_2$, which is reduced by alcoholic sodium sulphide to o-*picrylaminophenyl mercaptan*, $C_6H_2(NO_2)_3\cdot NH\cdot C_6H_4\cdot SH$. The latter, in which the picryl group must be attached to the nitrogen atom, is converted by warm aqueous sodium hydroxide into the same dinitrophenthiazine as results from the condensation of *o*-aminophenyl mercaptan and picryl chloride; consequently in this condensation the amino-, not the sulphydryl, group reacts with the chlorine atom of the picryl chloride.

3 : 5-Diaminophenazthionium chloride, acetic anhydride, and zinc chloride react to form a violet-black, crystalline *zincichloride*, from which 3-*amino*-5-*acetylaminophenazthionium chloride*,

$$C_6H_4\genfrac{}{}{0pt}{}{\diagup N \diagdown}{\diagdown SCl \diagup}C_6H_2(NH_2)\cdot NHAc,$$

can be obtained in violet needles; the corresponding *nitrate*, *platinichloride*, and *dichromate* are described, whilst the *base* itself, $C_{14}H_{11}ON_3S$, crystallises in brick-red needles.

In the hope of eliminating an amino-group, 3 : 5-diaminophenazthionium chloride, dissolved in moderately-concentrated sulphuric acid, has been treated with 10% sodium nitrite at 0°; however, the product, isolated as the *nitrate*, brownish-yellow needles, appears to be a diazonium salt of the annexed constitution from its analysis, explosiveness, and general behaviour. When treated with boiling water containing a little sulphuric acid, nitrogen is evolved, and a brownish-red *substance*, $C_{12}H_7ON_3S$, is obtained. C. S.



Preparation of 5 : 5-Dialkyliminobarbituric Acids (2-Imino-4 : 6-diketo-5-dialkylpyrimidines). EMANUEL MERCK (D.R.-P. 235802).—Dialkylmalonic esters react with guanidine in the presence of condensing agents to yield dialkylmalonylguanidines (5 : 5-dialkyliminobarbituric acids).

2-*Imino*-5 : 5-*diethylbarbituric acid*, $CEt_2<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>C:NH$, colourless needles, which on heating decompose without fusion, forms a crystalline *nitrate*, and on boiling with mineral acids furnishes diethylbarbituric acid, m. p. 191°. F. M. G. M.

1-Phenyl-5-methyl-1 : 2 : 4-triazole and Cyanophenylacetamidine. GUIDO PELLIZZARI (*Gazzetta*, 1911, **41**, ii, 93—100. Compare following abstract).—Bladin (Abstr., 1891, 472) described 1-phenyl-5-methyl-1 : 2 : 4-triazole (at first erroneously as 1-phenyl-3-methyl-1 : 2 : 4-triazole) as an uncrystallisable oil, b. p. about 250°, whilst Bamberger and Gruyter (Abstr., 1894, i, 23) recorded the same substance as a crystalline solid, m. p. 191°. The author has prepared 1-phenyl-5-methyl-1 : 2 : 4-triazole from formylphenylhydrazine and acetamide (compare following abstract), and finds that it is identical with the substance described by Bladin. The substance, m. p. 191°, of Bamberger and Gruyter is cyanophenylacetamidine,

$$NPh:CMe\cdot NH\cdot CN,$$

identical with that obtained from ethyl*iso*acetanilide and cyanamide by the method used by Comstock and Wheeler (Abstr., 1892, 747) for cyanophenylformamidine. Cyanophenylacetamidine has m. p. 193°. With warm potassium hydroxide it yields acetanilide and cyanamide. When treated with concentrated hydrochloric acid, it takes up water with formation of carbamidophenylacetamidine, $NPh:CMe\cdot NH\cdot CO\cdot NH_2$, which crystallises in lustrous plates, m. p. 180° (decomp.) if rapidly heated, or about 166° if slowly heated. R. V. S.

Triazole and its Derivatives. GUIDO PELLIZZARI (*Gazzetta*, 1911, **41**, ii, 20—42. Compare Abstr., 1895, i, 308 ; Pellizzari and Massa, Abstr., 1897, i, 205 ; 1901, i, 488).—The author gives a summary of the triazole derivatives which have been prepared by himself and his collaborators, and describes a number of other compounds obtained in the same way. Some of these have been prepared already by other investigators by different methods.

2-Phenyl-1 : 3 : 4-triazole (compare Young, Trans., 1901, **79**, 659) can be prepared from benzoylhydrazine and formamide, or from formylhydrazine and benzamide. The *hydrochloride*, $C_8H_7N_3,HCl$, forms colourless needles, m. p. 195°. The *platinichloride*,

$$(C_8H_7N_3)_2,H_2PtCl_6,2H_2O,$$

crystallises in orange-yellow plates, decomposing at 255°. Young obtained this salt with $3H_2O$. The platinic chloride compound, $(C_8H_7N_3)_2,PtCl_4$, obtained by boiling the preceding salt with water, is a yellow, flocculent substance.

2 : 5-Dimethyl-1 : 3 : 4-triazole (compare Stollé, Abstr., 1904, i, 453) can be prepared from acetylhydrazine and acetamide.

2 : 5-Diphenyl-1 : 3 : 4-triazole (compare Pinner, Abstr., 1894, i, 386) can be obtained from benzoylhydrazine and benzanilide.

1-Phenyl-3-methyl-1 : 2 : 4-triazole (compare Andreocci, Abstr., 1892, i, 636) is obtained, mixed with 1-phenyl-1 : 2 : 4-triazole and 1-phenyl-5-methyl-1 : 2 : 4-triazole, by the action of acetylphenylhydrazine on formamide. The 1-phenyl-1 : 2 : 4-triazole is separated with the aid of the insolubility of its *nitrate*, $C_8H_7N_3,HNO_3$, which forms white needles, m. p. 141°. 1-*Phenyl*-1 : 2 : 4-*triazole picrate*, $C_8H_7N_3,C_6H_3O_7N_3$, has m. p. 159°. 1-*Phenyl-3-methyl*-1 : 2 : 4-*triazole picrate*,

$$C_9H_9N_3,C_6H_3O_7N_3,$$

forms long, pale yellow needles, m. p. 171°.

1-Phenyl-5-methyl-1 : 2 : 4-triazole, b. p. 275° (compare preceding abstract), can be obtained from formylphenylhydrazine and acetamide. It is mixed with 1-phenyl-1 : 2 : 4-triazole and 1-phenyl-3-methyl-1 : 2 : 4-triazole, of which the former can be removed in the form of nitrate, and the latter by distillation. 1-*Phenyl*-5-*methyl*-1 : 2 : 4-*triazole picrate*, $C_9H_9N_3,C_6H_3O_7N_3$, forms short, prismatic crystals, m. p. 146°. The *platinichloride*, $(C_9H_9N_3)_2,H_2PtCl_6,2H_2O$, crystallises in yellow plates, m. p. 129° (decomp.). The *platinic chloride* compound, $(C_9H_9N_3)_2,PtCl_4$, is obtained as a pale yellow precipitate by boiling the preceding substance with water. 1-Phenyl-5-methyl-1 : 2 : 4-triazole yields the same methyltriazole as 1-phenyl-3-methyl-1 : 2 : 4-triazole (compare Andreocci, *loc. cit.*), so that there is only one 3-methyl-1 : 2 : 4-triazole.

1 : 3 : 5-Triphenyl-1 : 2 : 4-triazole (compare Engelhard, Abstr., 1897, i, 127) can be obtained: (1) from benzamide and β-benzoylphenylhydrazine; (2) from benzamide and α-benzoylphenylhydrazine; (3) from dibenzoylphenylhydrazine and ammonia. Its *hydrochloride* crystallises in needles, m. p. 174°.

1-*Phenyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole*, $C_{10}H_{11}N_3$, from acetamide and acetylphenylhydrazine, forms colourless crystals, m. p. 43°, b. p. 281°. The *platinichloride*, $(C_{10}H_{11}N_3)_2,H_2PtCl_6,2H_2O$, forms orange-coloured, acicular crystals, m. p. 185—186°; the anhydrous salt has m. p. 195°. The *picrate*, $C_{10}H_{11}N_3,C_6H_3O_7N_3$, crystallises in long, yellow needles, m. p. 156°.

1-*Phenyl*-2-*methyl*-1 : 3 : 4-*triazole*, $C_9H_9N_3$, from acetylphenylhydrazine and formanilide, forms laminar crystals (containing $1H_2O$), m. p. 68°; the anhydrous salt has m. p. 112°. The *picrate*, $C_9H_9N_3,C_6H_3O_7N_3$, has m. p. 134°. The *platinichloride*, $(C_9H_9N_3)_2,H_2PtCl_6$, crystallises in orange-coloured laminæ, m. p. 206°; when it is boiled with water the *platinic chloride* compound, $(C_9H_9N_3)_2,PtCl_4$, is obtained as a pale yellow precipitate. R. V. S.

Action of Acetyl Chloride on Acetylbiuret. ADRIANO OSTROGOVICH (*Gazzetta*, 1911, 41, ii, 70—74).—Further examination of the base obtained by the action of acetyl chloride on acetylbiuret (compare Abstr., 1898, i, 336) has shown that it is diketomethyltriazine (identical with that of Nencki, *Ber.*, 1876, 9, 234), formed by a dehydration analogous to that which occurs in the case of acetylguanylcarbamide (compare Abstr., 1909, i, 461):

$$COMe\cdot NH\cdot CO\cdot NH\cdot CO\cdot NH_2 = H_2O + NH<{CMe{=}N \atop CO\cdot NH}>CO.$$

This method is the most convenient for the synthesis of the substance, since it is only necessary to heat biuret with an excess of acetyl chloride for two or three hours at 100°, and then to raise the temperature to 140—145° for about four hours. R. V. S.

5-Aminopyrazoles and Iminopyrines. II. August Michaelis (*Annalen*, 1911, **385**, 1—43. Compare Abstr., 1905, i, 476).—The paper contains a description of the derivatives of 5-anilo- and 5-tolyl-iminopyrazolones (5-anilino- and 5-toluidino-pyrazoles). A general method of preparing these substances is the heating of the primary aromatic base and antipyrine chloride or the 2-methochlorides of other 5-chloropyrazoles at 200°.

5-*Anilo*-1-*phenyl*-3-*methylpyrazolone* (5-*anilino*-1-*phenyl*-3-*methylpyrazole*), $NPh{:}C\Big\langle\begin{matrix}NPh\cdot N\\ CH_2\cdot CMe\end{matrix}$ or $NHPh\cdot C\Big\langle\begin{matrix}NPh{:}N\\ CH-CMe\end{matrix}$, m. p. 120°, b. p. 365—366°, thus prepared from aniline and antipyrine chloride forms a *hydrochloride*, $C_{16}H_{15}N_3,HCl$, m. p. 118°, *platinichloride*, m. p. 135°, *hydriodide*, $C_{16}H_{15}N_3,HI,H_2O$, m. p. 110°, *nitrate*, m. p. 150°, and *hydrogen sulphate*, m. p. 153°. [With Felix Risse.]—It is converted by concentrated hydrochloric acid and sodium nitrite in a freezing mixture into 4-*oximino*-5-*anilo*-1-*phenyl*-3-*methylpyrazolone* (4-*nitroso*-5-*anilino*-1-*phenyl*-3-*methylpyrazole*), m. p. 168°, deep green needles (*hydrochloride*, $C_{16}H_{14}ON_4,HCl$, yellow needles). This nitroso-compound is unstable in solution, readily changing to the isomeric 3 : 4-*diphenyl*-6-*methyldihydropyrazofurazan*, $N\Big\langle\begin{matrix}NPh\cdot C\cdot NPh\\ CMe\cdot C-NH\end{matrix}\Big\rangle O$, m. p. 157°, yellow needles, which is also obtained by the action of concentrated hydrochloric acid and sodium nitrite (in small excess) on 5-anilino 1-phenyl-3-methylpyrazole at a moderate temperature.

4-*Amino*-5-*anilino*-1-*phenyl* - 3 - *methylpyrazole*, $C_{16}H_{16}N_4$, m. p. 140—141°, white needles, obtained by the reduction of the nitroso-compound, forms a *hydrochloride*, m. p. 240°, *phenylcarbamide*, m. p. 220°, *phenylthiocarbamide*, m. p. 160°, and *acetyl* derivative, m. p. 130 (decomp.), and is converted by sodium nitrite and warm dilute acetic acid into 3 : 4-*diphenyl*-6-*methylaziminopyrazole*,

$$N\Big\langle\begin{matrix}NPh\cdot C\cdot NPh\\ CMe\cdot C-\!\!-N\end{matrix}\Big\rangle N,$$

white needles, m. p. 152°.

5-p-*Nitroanilino*-1-*phenyl*-3-*methylpyrazolone*,

$$NO_2\cdot C_6H_4\cdot N{:}C\Big\langle\begin{matrix}NPh\cdot N\\ CH_2-CMe\end{matrix},$$

yellow needles, m. p. 153°, can be obtained in bad yield by the action of concentrated nitric acid on the anilophenylmethylpyrazolone, but is best prepared by heating 2 : 5-*p*-nitroanilopyrine hydrochloride or hydriodide (following abstract); the m-*nitro*-isomeride, m. p. 138°, has been obtained by a method similar to the latter.

[With Fritz Isert.]—5-*Anilo*-1-p-*bromophenyl*-3-*methylpyrazolone*, $C_{16}H_{14}N_3Br$, m. p. 106°, is obtained by distilling *p*-bromoanilopyrine (2 : 5-*endo*anilo-1-*p*-bromophenyl-2 : 3-dimethylpyrazole) hydro-

chloride (following abstract) under 11 mm. pressure, or by heating aniline and 5-chloro-1-*p*-bromophenyl-3-methylpyrazole-2-methochloride at 200°; the corresponding p-*chloro*-compound has m. p. 94°.

[With W. THOMAS.]—5-p-*Bromoanilo*-1-*phenyl*-3-*methylpyrazolone*, m. p. 136°, and the corresponding *chloro*-compound, m. p. 139°, are obtained by methods similar to the preceding. The action of bromine (3 mols.) in acetic acid on 5-anilo-1-phenyl-3-methylpyrazolone produces a tribrominated *substance*, m. p. 131° (4-*bromo*-5-*bromoanilo*-1-*bromophenyl*-3-*methylpyrazolone* ?), which certainly contains a bromine atom in position 4, since it is unattacked by nitrous acid.

[With FELIX RISSE.]—5-*Anilo*-1-*phenyl*-4-*benzylidene*-3-*methylpyrazolone*, m. p. 164°, yellow prisms, and the corresponding *anisylidene* derivative, m. p. 205°, yellow needles, are prepared by heating the anilophenylmethylpyrazolone and benzaldehyde or anisaldehyde with zinc chloride at 125° for four to five hours.

[With FELIX ABRAHAM.]—The reduction of 4-nitroso-5-methylanilino-1-phenyl-3-methylpyrazole (4-nitroso-ψ-anilopyrine) (Abstr., 1908, i, 61) yields 4-*amino*-5-*methylanilino*-1-*phenyl*-3-*methylpyrazole*,

$$NMePh\cdot C\begin{cases}NPh — N \\ C(NH_2)\cdot CMe\end{cases},$$

m. p. 85°, which forms a *hydrochloride*, m. p. 197°, *benzylidene* derivative, m. p. 101° (by means of which the base is best purified), *salicylidene* derivative, m. p. 133°, *cinnamylidene* derivative, m. p. 114°, *benzoyl* derivative, m. p. 167°, and *carbamide*, $C_{17}H_{16}N_3\cdot NH\cdot CO\cdot NH_2$, m. p. 193°. By diazotisation, 4-amino-ψ-anilopyrine yields a stable, crystalline *diazo*-ψ-*anilopyrine chloride*, which couples with β-naphthol to form a red, crystalline *substance*, $C_{17}H_{16}N_3\cdot N_2\cdot C_{10}H_6\cdot OH$, m. p. 173°. 4-*Amino*-5-*ethylanilino*-1-*phenyl*-3-*methylpyrazole* (4-*amino*-ψ-*ethylanilopyrine*), obtained by the reduction of 4-nitroso-ψ-ethylanilopyrine (Abstr., 1908, i, 61), crystallises in white leaflets, has m. p. 129·5°, and forms a *hydrochloride*, $C_{18}H_{20}N_4,HCl$, m. p. 220°, and *benzoyl* derivative, m. p. 208°. 5-Anilino-1-phenyl-3-methylpyrazole cannot be acetylated (or alkylated) directly, but 5-*acetylanilino*-1-*phenyl*-3-*methylpyrazole*, $NPhAc\cdot C\begin{cases}NPh\cdot N \\ CH—CMe\end{cases}$, m. p. 96°, can be prepared by distilling a solution of anilopyrine in chloroform with acetyl chloride, at first under ordinary, and finally under reduced, pressure.

5-p-*Nitromethylanilino*-1-*phenyl*-3-*methylpyrazole*,

$$NO_2\cdot C_6H_4\cdot NMe\cdot C\begin{cases}NPh\cdot N \\ CH—CMe\end{cases},$$

m. p. 174°, and the meta-*isomeride*, m. p. 125°, form stout, yellow crystals, and are prepared by heating the methiodides of the corresponding 2:5-nitroanilopyrines. 5-p-*Chloromethylanilino*-1-*phenyl*-3-*methylpyrazole* and the corresponding *p*-bromo-*compound* have m. p. 61° and 84° respectively, whilst the isomeric 5-*anilino*-1-p-*chlorophenyl*-2:3-*dimethylpyrazole* and 5-*anilino*-1-p-*bromophenyl*-2:3-*dimethylpyrazole* have m. p. 126° and 120° respectively.

[With FRIEDRICH WALTER.]—5-*Anilo*-1-*phenylpyrazolone*,

$$NPh:C\begin{cases}NPh\cdot N \\ CH_2—CH\end{cases},$$

m. p. 138°, is prepared by heating 5-chloro-1-phenylpyrazole-2-meth-

iodide (following abstract) with aniline (2 mols.) at 200°, forms a green, crystalline 4-*oximino*-(or *nitroso*-)-compound, m. p. 113°, and yields a *methiodide* (identical with 2 : 5-anilo-1-phenyl-2-methylpyrazole hydriodide [following abstract]) with methyl iodide at 110—120°, an *ethiodide*, m. p. 149°, and a *propiodide*, m. p. 165°. 5-*Methylanilino*-1-*phenylpyrazole*, m. p. 51°, prepared by heating 5-anilo-1-phenyl-2-methylpyrazole methiodide under 13 mm. pressure, forms a stable, dark green 4-*nitroso*-derivative, m. p. 99°.

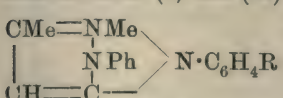
[With F. Risse.]—5-p-*Tolylimino*-1-*phenyl*-3-*methylpyrazolone*,

$$C_7H_7\cdot N{:}C{<}\begin{matrix}NPh\cdot N\\ \quad\ \ \| \\ CH_2-CMe\end{matrix},$$

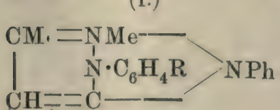
m. p. 109°, is prepared by heating 2 : 5-*p*-tolylimino-1-phenylpyrine hydriodide (following abstract) under 15—20 mm. pressure, or, better, by heating antipyrine chloride and *p*-toluidine (2 mols.) at 200°. Its 4-*oximino*-derivative, m. p. 117°, dark green leaflets, forms a reddish-yellow *hydrochloride*, $C_{17}H_{16}ON_4,HCl$, m. p. 152°, and yields by reduction 4-*amino*-5-p-*toluidino*-1-*phenyl*-3-*methylpyrazole*, m. p. 131° (*hydrochloride*, m. p. 241—242°; *acetyl* derivative, m. p. 193°; *azoimido*-compound, m. p. 111—112°). 4-*Phenyl*-3-p-*tolyl*-6-*methyldihydropyrazofurazan*, $N{<}\begin{matrix}NPh\cdot C\cdot N(C_7H_7)\\ \quad\ \| \\ CMe\cdot C\cdot NH\text{———}\end{matrix}{>}O$, obtained by intramolecular change from the preceding oximino-compound, forms yellow needles, m. p. 176°. 5-*p*-Tolylimino-1-phenyl-3-methylpyrazolone condenses with benzaldehyde and with anisaldehyde in the presence of zinc chloride to form the *benzylidene* and *anisylidene* derivatives, m. p. 163° and 184° respectively.

5-*Anilo*-1-p-*tolyl*-3-*methylpyrazolone*, m. p. 106°, and the corresponding o-*tolyl* compound, m. p. 131°, are obtained by heating the hydriodides of the respective tolylanilopyrines (following abstract). 5-*Methylanilino*-1-p-*tolyl*-3-*methylpyrazole*, m. p. 96°, forms a *hydrochloride*, m. p. 133·5°, and *platinichloride*, m. p. 189°. 5-*Methylanilino*-1-o-*tolyl*-3-*methylpyrazole* has m. p. 67°. 5-*Acetylanilino*-1-p-*tolyl*-3-*methylpyrazole*, $NAcPh\cdot C{<}\begin{matrix}N(C_7H_7)\cdot N\\ \qquad\quad\ \| \\ CH\text{———}CMe\end{matrix}$, and the corresponding *benzoyl* derivative have m. p. 84° and 114° respectively. C. S.

Substituted Iminopyrines. August Michaelis (*Annalen*, 1911, 385, 44—102. Compare preceding abstract).—The chief object of the research is an investigation of various iminopyrines and their derivatives, in order to show that the substances represented by the constitutions (I) and (II) are isomeric and not identical.



(I.)



(II.)

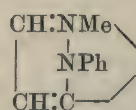
[With Friedrich Walter.]—5-*Chloro*-1-*phenylpyrazole*-3-*carboxylic acid*,

$$CO_2H\cdot C{<}\begin{matrix}N—NPh\\ CH{:}CCl\end{matrix},$$

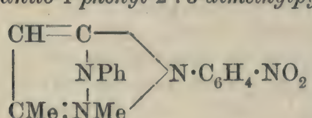
m. p. 158° (*ethyl* ester, m. p. 46°; *chloride*, m. p. 96°), is obtained by heating ethyl 1-phenyl-5-pyrazolone-3-carboxylate with phosphoryl chloride and benzene at 160—170°. The action of chlorine or bromine on its acetic acid solution yields

4 : 5-*dichloro*-1-*phenylpyrazole*-3-*carboxylic acid*, m. p. 214°, and 5-*chloro*-4-*bromo*-1-*phenylpyrazole*-3-*carboxylic acid*, m. p. 222°, respectively. When heated at 200—210°, the chlorophenylpyrazolecarboxylic acid yields 5-chloro-1-phenylpyrazole, which is also conveniently prepared by heating 1-phenyl-5-pyrazolone and phosphoryl chloride at 140—150°. The bromination of 5-chloro-1-phenylpyrazole in acetic acid yields 5-*chloro*-4-*bromo*-1-*phenylpyrazole*, m. p. 65° ; 4 : 5-*dichloro*-1-*phenylpyrazole*, m. p. 48°, which cannot be prepared in a similar manner, is obtained by heating 5-chloro-1-phenylpyrazole and phosphorus pentachloride at 150—160°. 3 : 4 : 5-*Trichloro*-1-*phenylpyrazole*, m. p. 82°, is prepared by chlorinating Michaelis and Rohmer's 3 : 5-dichloro-1-phenylpyrazole in chloroform or by heating it with phosphorus pentachloride at 150°. 3 : 5-*Dichloro*-4-*bromo*-1-*phenylpyrazole*, m. p. 85°, is prepared by brominating the dichlorophenylpyrazole. 3 : 5-*Dibromo*-1-*phenylpyrazole*, m. p. 50°, prepared by heating 3-hydroxy-1-phenyl-5-pyrazolone (Michaelis and Schenk, Abstr., 1907, i, 966) with phosphoryl bromide at 120—130°, yields 3 : 4 : 5-*tribromo*-1-*phenylpyrazole*, m. p. 122°, by bromination in boiling acetic acid.

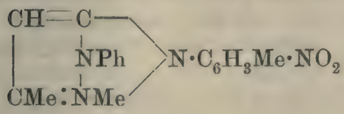
5-*Chloro*-1-*phenylpyrazole* 2-*methiodide*, $NPh<\begin{matrix}CCl{=}CH\\N(MeI){:}CH\end{matrix}$, m. p. 161° (decomp.), is obtained from its constituents and a little methyl alcohol at 100°. The corresponding *methochloride*, m. p. 147°, forms a *platinichloride*, $2C_{10}H_{10}N_2Cl,PtCl_6,H_2O$, m. p. 207°, and a *picrate*, m. p. 106°. The *ethiodide*, m. p. 209°, *ethochloride*, m. p. 181° (*platinichloride*, m. p. 217°), and *propiodide*, m. p. 156° (decomp.), are also mentioned.

2 : 5-*Anilo*-1-*phenyl*-2-*methylpyrazole*,  >NPh, m. p. 128°, prepared by the general method of heating 5-chloropyrazole-2-alkyliodides and primary aromatic bases (preceding abstract), forms a *hydrochloride*, *platinichloride*, m. p. 177°, *hydriodide*, m. p. 161° (identical with 5-anilo-1-phenylpyrazolone-2-methiodide [preceding abstract]), *thiocyanate*, m. p. 137°, *picrate*, m. p. 104°, *methiodide*, $\begin{matrix}CH{=}C(MeI)\\CH{:}C(NPhMe)\end{matrix}>NPh$, m. p. 124—125°, *ethiodide*, m. p. 146°, and *benzoyl iodide*, $C_{16}H_{15}N_3,C_6H_5\cdot COI$, m. p. 108°. 2 : 5-*Anilo*-1-*phenyl*-2-*ethylpyrazole*, m. p. 155°, and 2 : 5-*anilo*-1-*phenyl*-2-*propylpyrazole*, m. p. 124·5°, are prepared by the general method ; the former forms a *platinichloride*, m. p. 197°, *hydriodide*, m. p. 149°, *picrate*, m. p. 172°, and *methiodide*, m. p. 119°, whilst the *platinichloride* and *hydriodide* of the latter have m. p. 195° and 165° respectively.

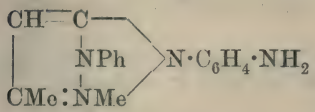
[With ERICH WURL and FELIX DOEPMANN.]—2 : 5-m-*Nitroanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole* (2 : 5-m-*nitroanilopyrine*) (annexed formula), m. p. 114°, garnet-red crystals, and 2 : 5-p-*nitroanilopyrine*, m. p. 129°, dark red crystals with a green shimmer, are obtained from antipyrine chloride and the nitroanilines



by the general method. The former forms a *platinichloride*, $2C_{17}H_{16}O_2N_4,H_2PtCl_6,3\frac{1}{2}H_2O$, m. p. 204° (decomp.), *hydriodide*, m. p.



(I.)



(II.)

164°, *methiodide*, m. p. 144°, *acetyl iodide*, m. p. 196° (decomp.), and *benzoyl iodide*, m. p. 178°, whilst 2 : 5-*p*-nitroanilopyrine forms a *platinichloride*, m. p. 217°, *hydriodide*, m. p. 198° (decomp.), and *methiodide*, m. p. 194° (decomp.) (compare this vol., i, 232, for the isomeric nitro-anilopyrines and their derivatives). 2 : 5-o-*Nitro*-p-*tolylimino*-1-*phenyl*-2 : 3-*dimethylpyrazole* (formula I), m. p. 100°, stout, red crystals, forms a *platinichloride*, m. p. 131°, and *picrate*, m. p. 145°.

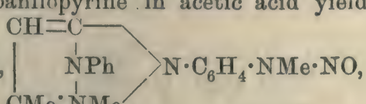
2 : 5-m-*Aminoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole* (formula II), m. p. 45—50°, can be prepared by reducing the nitro-compound, but is far more conveniently obtained by heating antipyrine chloride and acetyl-*m*-phenylenediamine at 125—130° and hydrolysing the resulting *acetyl* derivative, m. p. 212°. It forms a *dihydrochloride*,

$$C_{17}H_{18}N_4,2HCl,$$

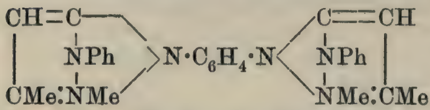
decomp. 260°, *platinichloride*, decomp. 227°, *benzoyl* derivative, m. p. 172°, and *benzoyl iodide*, m. p. 218°, the *hydrochloride*,

$$C_{24}H_{23}ON_4I,HCl,$$

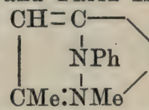
of which has m. p. 222°. 2 : 5-p-*Aminoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, m. p. 112°, prepared by similar methods as the meta-isomeride, forms a *dihydrochloride*, m. p. 245°, and an *acetyl* derivative, m. p. 196°, the *hydriodide* of which has m. p. 151°.

as-Dimethyl-*p*-phenylenediamine and antipyrine chloride react best at 125° to form 2 : 5-p-*dimethylaminoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, m. p. 120°, green plates or greenish-yellow prisms, which is a very strong base, absorbs carbon dioxide, and forms two series of salts, according as one equivalent of an acid combines with the dimethylamino-group, or as yet another equivalent breaks the bridge; the former salts are green, faintly alkaline, and contain H_2O, whilst the latter are colourless, faintly acidic, and anhydrous. The *dihydrochloride*, m. p. 224°, *dihydriodide*, m. p. 208°, *hydrochloride*, m. p. 116°, *hydriodide*, m. p. 72—73°, *dimethiodide*, m. p. 205°, and *methiodide*, m. p. 153°, are described. The action of sodium nitrite (3 mols.) on 2 : 5-*p*-dimethylaminoanilopyrine in acetic acid yields formaldehyde and the *nitrosoamine*,  m. p. 169°, orange-yellow leaflets, which is converted by reduction into 2 : 5-p-*methylaminoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, m. p. 143°, sulphur-yellow needles (*acetyl* derivative, m. p. 142°). The *nitrosoamine*, m. p. 164°, dark red needles (*hydriodide*, m. p. 192°), of 4-nitro-2 : 5-*p*-methylaminoanilo-1-phenyl-2:3-dimethylpyrazole is obtained by passing nitrous fumes into an alcoholic solution of the preceding nitrosoamine containing a little acetic acid.

m-*Phenylenebis*-2 : 5-*imino*-1-*phenyl*-2 : 3-*dimethylpyrazole* (annexed formula), m. p. 204°, yellowish-white crystals, is obtained by heating *m*-phenylenediamine and antipyrine chloride at 130—135°, and forms a *platinichloride*, decomp. 300°, *dihydriodide*, m. p. 203°, and *dimethiodide*, m. p. 154°.

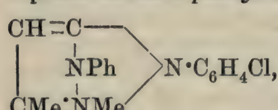


[With WILHELM THOMAS and FRITZ ISERT.]—2 : 5-p-*Chloroanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*,



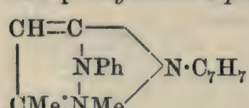
m. p. 78°, yellow prisms, is obtained by heating *p*-chloroaniline (2 mols.) and antipyrine chloride or 5-chloro-1-phenyl-3-methylpyrazole-2-methiodide on the water-bath. It forms a *hydrochloride*, *platinichloride*, m. p. 89° (decomp. in its $6H_2O$ of crystallisation), *hydriodide*, m. p. 180°, *picrate*, m. p. 147°, *methiodide*, m. p. 192°, *ethiodide*, m. p. 172°, and *benzoyl iodide*, m. p. 183°. 2 : 5-m : p-*Dichloroanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, a yellow oil (*picrate*, m. p. 152°; *methiodide*, m. p. 191°), 2 : 5-p-*bromoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, m. p. 81° (*platinichloride*, m. p. 115°; *hydriodide*, m. p. 206°; *picrate*, m. p. 159°; *methiodide*, m. p. 193°; *ethiodide*, m. p. 176°), and 2 : 5-m-*bromoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, a yellow oil (*platinichloride*, m. p. 211°; *hydriodide*, m. p. 205°; *picrate*, m. p. 190°; *methiodide*, m. p. 133°; *ethiodide*, m. p. 118°), have also been prepared.

1-p-*Chlorophenyl*-3-*methyl*-5-*pyrazolone*, m. p. 88°, is obtained by heating equal molecular quantities of *p*-chlorophenylhydrazine and ethyl acetoacetate in 50% acetic acid at 100°. Its *methiodide*, m. p. 233° (decomp.), reacts with an excess of aniline at 110° to form 1-p-*chloroanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole* (annexed formula), m. p. 96°, yellow needles (*hydrochloride*, m. p. 200°; *platinichloride*, m. p. 199°; *hydriodide*, m. p. 189°; *picrate*, m. p. 192°; *methiodide*, m. p. 70° [hydrated] or 159° [anhydrous]; *methochloride*, m. p. 155°).



1-p-*Bromoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, m. p. 119°, forms a *hydrochloride*, m. p. 202—203°, *platinichloride*, decomp. 202°, *aurichloride*, m. p. 166°, *hydriodide*, m. p. 176°, *picrate*, m. p. 193°, *methochloride*, m. p. 157°, and *methiodide*, m. p. 101° (hydrated) and 158° (anhydrous).

[With WALDEMAR MENTZEL.]—The 2 : 5-tolylimino-1-phenyl-2 : 3-dimethylpyrazoles have been prepared by the general method from antipyrine chloride and *o*- or *p*-toluidine (2 mols.) at 125°. 2 : 5-p-*Tolylimino*-1-*phenyl*-2 : 3-*dimethylpyrazole* (annexed formula), m. p. 106°, white leaflets, forms a *hydrochloride*, m. p. 207°, *platinichloride*, m. p. 138°, *hydriodide*, m. p. 166°, *picrate*, m. p. 144°, *methiodide*, m. p. 187°, *acetyl iodide*, m. p. 166°, and *benzoyl iodide*, m. p. 207°. 2 : 5-o-*Tolyl*-



imino-1-*phenyl*-2 : 3-*dimethylpyrazole*, m. p. 69°, forms a *hydriodide*, m. p. 157°, and *methiodide*, m. p. 192°. The isomeric 1-*p*- and *o*-tolylanilopyrines have been prepared from aniline (2 mols.) and 1-*p*- or *o*-tolylantipyrine chloride at 125°. 2 : 5-*Anilo*-1-p-*tolyl*-2 : 3-*dimethylpyrazole*, m. p. 106°, forms a *platinichloride*, m. p. 210°, *hydriodide*, m. p. 165·5°, *picrate*, m. p. 169°, *methiodide*, m. p. 175°, *acetyl iodide*, m. p. 206°, and *benzoyl iodide*, m. p. 147°, whilst 2 : 5-*anilo*-1-o-*tolyl*-2 : 3-*dimethylpyrazole*, m. p. 129°, yields a *hydriodide*, m. p. 196°, and *methiodide*, m. p. 167°. C. S.

Ethyl Arylazoacetonedicarboxylates and their Isomeric Condensation Products with Hydrazines. CARL BÜLOW and HERMANN GÖLLER (*Ber.*, 1911, **44**, 2835—2847).—The reaction between a diazonium salt and ethyl acetonedicarboxylate in cold aqueous alcohol in the presence of sodium acetate yields *ethyl arylazoacetonedicarboxylates*, $R\cdot N_2\cdot CH(CO_2Et)\cdot CO\cdot CH_2\cdot CO_2Et$, which are yellow, crystalline substances soluble in dilute alkalis: R = Ph, m. p. 48·5°; $R = o\text{-}C_7H_7$, m. p. 80—85°, decomp. 195°; $R = p\text{-}C_7H_7$, m. p. 81—81·5°; $R = m\text{-}C_6H_3Me_2$, m. p. 71—72°; $R = o\text{-}C_6H_4\cdot CO_2H$, m. p. 145—146°. These substances react with phenylhydrazine in glacial acetic acid at the ordinary temperature to form *ethyl* 5-*hydroxy*-1-*phenylpyrazole*-3-*glyoxylate-arylhydrazones*,

$$\begin{matrix} \mathrm{NPh\cdot N} \\ \mathrm{OH\cdot C{=\!=}CH} \end{matrix}\!\!>\mathrm{C\cdot C(CO_2Et){:}N\cdot NHR};$$

R = Ph, m. p. 137—138°; $R = o\text{-}C_7H_7$, m. p. 171° (decomp.); $R = p\text{-}C_7H_7$, m. p. 170—171° (decomp.); $R = m\text{-}C_6H_3Me_2$, m. p. 151°; $R = o\text{-}C_6H_4\cdot CO_2H$, m. p. 218—219° (decomp.). These compounds, which are yellow and crystalline, are given the constitution stated, because they respond to the Bülow reaction, and are soluble in dilute alkalis or aqueous piperidine. In a similar manner, the ethyl arylazoacetonedicarboxylates react with 60% hydrazine hydrate to form yellow, crystalline ethyl 5-hydroxypyrazole-3-glyoxylate-arylhydrazones, $\begin{matrix} \mathrm{NH{-\!-\!-}N} \\ \mathrm{C(OH){:}CH} \end{matrix}\!\!>\mathrm{C\cdot C(CO_2Et){:}N\cdot NHR}$; R = Ph, m. p. 170—171° (decomp.); $R = o\text{-}C_7H_7$, m. p. 162°; $R = p\text{-}C_7H_7$, m. p. 180—181° (decomp.); $R = m\text{-}C_6H_3Me_2$, m. p. 207—208° (decomp.); $R = o\text{-}C_6H_4\cdot CO_2H$, decomp. 255°, darkening at 235°.

The two preceding groups of compounds are isomeric with the ethyl 4-arylazo-5-hydroxy-1-phenylpyrazole-3-acetates or ethyl 4-arylazo-5-hydroxypyrazole-3-acetates obtained by condensing ethyl 5-hydroxy-1-phenylpyrazole-3-acetates or ethyl 5-hydroxypyrazole-3-acetates respectively with diazonium salts in the presence of sodium acetate; thus ethyl 5-hydroxy-1-phenylpyrazole-3-acetate and *p*-toluenediazonium chloride yield *ethyl* 4-p-*tolueneazo*-5-*hydroxy*-1-*phenylpyrazole*-3-*acetate*, $\mathrm{NPh}\!<\!\begin{matrix} \mathrm{N{=\!=\!=}C\cdot CH_2\cdot CO_2Et} \\ \mathrm{C(OH){:}C\cdot N_2\cdot C_7H_7} \end{matrix}$, m. p. 132—134°, orange needles, which is soluble in dilute alkalis or aqueous piperidine; its constitution is proved by the fact that the *acid*, obtained by its hydrolysis by 10% alkali, loses carbon dioxide at 175—180°, yielding Lapworth's 4-*p*-tolueneazo-5-hydroxy-1-phenyl-3-methylpyrazole. The constitution of

ethyl 4-*p*-nitrobenzeneazo-5-hydroxy-1-phenylpyrazole-3-acetate, prepared by the preceding or by Bülow and Höpfner's method (Abstr., 1901, i, 239), has been similarly proved by converting the substance into 4-*p*-nitrobenzeneazo-5-hydroxy-1-phenyl-3-methylpyrazole. C. S.

Quadriurates. WILHELM E. RINGER (*Zeitsch. physiol. Chem.*, 1911, 75, 13—18. Compare Kohler, this vol., i, 243, 690; also Ringer, Abstr., 1910, ii, 838).—It is considered that the non-existence of quadriurates has not been proved as yet. The possibility of the formation of mixed crystals of urates and uric acid is suggested. On cooling such a mixture, the solid would remain in presence of its mother liquor for a time, although not in equilibrium with it, and still less in equilibrium with water. In time, decomposition and liberation of part of the uric acid would take place. The mixed crystals formed on evaporation at a constant temperature are in equilibrium with the mother liquors; they therefore do not decompose when kept, and decompose only very slowly in presence of water at the same temperature. Such substances would correspond in composition with the quadriurates without being true chemical compounds. E. F. A.

Benziminazoles and Benzoxazoles and Azo-dyes Derived Therefrom. OTTO KYM and S. KOWARSKI (*Ber.*, 1911, 44, 2919—2932. Compare Abstr., 1904, i, 453).—The effect on the colour and affinity for vegetable fibres of an increasing number of amino-groups in azo-dyes of this class has been investigated already, and in this paper the effect in this direction of introducing (*a*) a second iminazole group or (*b*) a second oxazole group, is shown to be the production of a red tone in the dye, with no increase in the affinity for cotton.

3-*Nitro*-1 : 4-*di*-p-*nitrobenzoyl*-p-*phenylenediamine*,

$$NO_2\cdot C_6H_3(NH\cdot CO\cdot C_6H_4\cdot NO_2)_2,$$

m. p. above 305°, prepared by the action of *p*-nitrobenzoyl chloride on either nitro-*p*-phenylenediamine or nitrodiacetyl-*p*-phenylenediamine, crystallises from pyridine on adding hot alcohol in glancing, golden-yellow leaflets. On nitration with fuming nitric acid, it gives 2 : 3-*dinitro*-1 : 4-*di*-p-*nitrobenzoyl*-p-*phenylenediamine*, m. p. 262°, which may also be obtained by the action of *p*-nitrobenzoyl chloride on dinitrodiacetyl-*p*-phenylenediamine. This crystallises from acetone on addition of water in small, yellow needles, is much more soluble in organic solvents than the mononitro-compound, and on reduction with tin and hydrochloric acid furnishes the corresponding 2 : 5-*di*-p-*aminophenyl*-o-*benzdi-iminazole*,

$$NH_2\cdot C_6H_4\cdot C{<}\begin{matrix}NH\cdot C\cdot CH\cdot CH\cdot C\cdot NH\\ N{-}C{-}{-}{-}{-}{-}C{-}N\end{matrix}{>}C\cdot C_6H_4\cdot NH_2,$$

which sinters at 230°, losing water of crystallisation, and then melts at 255°; it crystallises from pyridine on addition of water in bright brown, glancing needles, and shows a bluish-violet fluorescence in all solutions. The *diacetyl* derivative is colourless and practically insoluble in all solvents.

4 : 6-*Dinitroresorcinyl di*-p-*nitrobenzoate*, m. p. 178°, prepared by treating dinitroresorcinol with *p*-nitrobenzoyl chloride, crystallises in

slender, yellowish-brown needles from boiling acetic acid on addition of water, and is insoluble in acetone or pyridine, but appears to undergo change in the latter solvent, since addition of water causes the separation of an intensely yellow jelly. On reduction with stannous chloride, tin, and hydrochloric acid, it furnishes a 5% yield of 1 : 5-*di*-p-*aminophenylbenzdioxazole*,

$$NH_2\cdot C_6H_4\cdot C{<}{}^{O}_{N}{>}C_6H_2{<}{}^{O}_{N}{>}C\cdot C_6H_4\cdot NH_2,$$

which sinters at 170° and remains unchanged on further heating, crystallises from hot acetone on addition of water in small, brown needles, and shows a bluish-violet fluorescence in alcohol. The same substance was obtained in larger yield in the following series of reactions.

When 4 : 6-diaminoresorcinol hydrochloride is heated with *p*-nitrobenzoyl chloride in xylene solution, *di*-p-*nitrobenzoylaminoresorcinol*, $C_6H_2(OH)_2(NH\cdot CO\cdot C_6H_4\cdot NO_2)_2$, is obtained as an orange-coloured, insoluble, sandy powder, which does not melt at 300°, but on heating at 260—270° is converted into 1 : 5-*di-p-nitrophenylbenzdioxazole*, which alone is formed if the initial reaction is carried out in nitrobenzene solution instead of xylene, This has m. p. above 300°, forms small, bright yellow needles, and is insoluble in acids or alkalis, but can be recrystallised from nitrobenzene. On reduction by heating with zinc dust and acetic acid, it gave the corresponding 1 : 5-di-*p*-aminophenylbenzdioxazole described above.

The diaminobenzdi-iminazole and diaminobenzdioxazole bases here described were diazotised and coupled with aminonaphtholdisulphonic acid, β-naphtholdisulphonic acid, and α-naphthol, and gave in each case dyes which on cotton furnished colours distinctly redder in shade than those given by the corresponding products from the monoiminazole and mono-oxazole respectively. T. A. H.

Azoxy-compounds. Angelo Angeli and Luigi Alessandri (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 170—176. Compare this vol., i, 817).—The *p*-nitroazoxybenzene of Zinin is unaltered when treated with nitric acid (D 1·48) for four minutes at room temperature (27°), whilst under these conditions the compound of m. p. 148° (now given as 149°), previously described, yields 4 : 4′-dinitroazoxybenzene, which is only formed from Zinin's compound when the action of the nitric acid is prolonged. Both substances remain unaltered when treated with bromine in glacial acetic acid, but if they are mixed with a little iodine and added to bromine, Zinin's compound is unacted on, whilst from the other a *bromo*-derivative is produced, crystallising in yellow prisms, m. p. 199°. Azoxybenzene in similar circumstances gives a *bromo*-derivative, m. p. 75°. R. V. S.

Action of Phosphorus Pentachloride on the Azoxy-compounds. G. Charrier and G. Ferreri (*Atti R. Accad. Sci. Torino*, 1911, 46, 1009—1023).—The authors have studied the action of phosphorus pentachloride on the azoxy-compounds obtained by uniting β-naphthol with *o*- and *p*-methoxyphenyldiazonium chloride, and with *o*- and *p*-ethoxyphenyldiazonium chloride. They find that in the case of

the compounds from *p*-anisidine and *p*-phenetidine, the hydroxyl group is substituted by chlorine. The derivatives of *o*-anisidine and *o*-phenetidine, however, behave differently; hydrogen chloride and methyl or ethyl chloride are evolved, and a compound containing phosphorus and chlorine is obtained, for which the formula $\begin{matrix} N\cdot C_6H_4-O \\ \| \\ N\cdot C_{10}H_6\cdot O \end{matrix}{>}PCl_3$ is suggested. This substance yields *o*-hydroxybenzeneazo-β-naphthol when treated with water. In addition, all the azoxy-compounds give small quantities of infusible substances containing phosphorus.

o-*Methoxybenzeneazo-β-naphthol*, $OH\cdot C_{10}H_6\cdot N\colon N\cdot C_6H_4\cdot OMe$, forms yellowish-red needles, m. p. 178°. It dissolves in concentrated sulphuric acid, giving a reddish-violet coloration.

o-*Ethoxybenzeneazo-β-naphthol*, $C_{18}H_{16}O_2N_2$, crystallises in minute, orange-red leaves, m. p. 138°. It gives a reddish-violet coloration with concentrated sulphuric acid.

o-Hydroxybenzeneazo-β-naphthol crystalises in three forms: (1) green tablets (from ethyl alcohol and ethyl acetate); (2) in crusts of small, red needles (from benzene and toluene); (3) red needles with a golden lustre (from methyl alcohol). The last two forms change into the first in contact with alcohol or on heating. The *sodium* salt, $C_{16}H_{11}O_2N_2Na,3H_2O$, and the *potassium* salt, $C_{16}H_{11}O_2N_2K,1\frac{1}{2}H_2O$, which both crystallise in green scales, were prepared. The *acetyl* derivative, $C_{18}H_{14}O_3N_2$, forms ruby-red needles, m. p. 153°. The *benzoyl* derivative, $C_{23}H_{16}O_3N_2$, forms small, orange-yellow needles, m. p. 216°. The *benzyl* derivative, $C_{23}H_{18}O_2N_2$, crystallises in small, red needles, m. p. 152—153°.

p-*Methoxybenzeneazo-β-naphthol*, $C_{17}H_{14}O_2N_2$, forms red needles, m. p. 137°. It dissolves in concentrated sulphuric acid, giving a reddish-violet coloration, and is reprecipitated on addition of water. When it is heated with an equimolecular quantity of phosphorus pentachloride on the water-bath, 1-p-*methoxybenzeneazo*-2-*chloronaphthalene*, $C_{10}H_6Cl\cdot N\colon N\cdot C_6H_4\cdot OMe$, is produced; it crystallises in small, orange-red prisms or lustrous, reddish-yellow scales, m. p. 87°. It gives a reddish-violet coloration with concentrated sulphuric acid. On reduction with zinc and acetic acid, it yields *p*-anisidine and 2-chloro-1-naphthylamine, of which the *monoacetyl* derivative, $C_{12}H_{10}ONCl$, crystallises in colourless needles, m. p. 191°, and the *diacetyl* derivative, $C_{14}H_{12}O_2NCl$, forms colourless prisms, m. p. 88°. With nitrous acid, 2-chloro-1-naphthylamine yields in solution 2-*chloro*-1-*naphthyldiazonium chloride*, which reacts with β-naphthylamine to form 2-*chloro*-1-*naphthaleneazo*-2′-*naphthylamine*, $C_{10}H_6Cl\cdot N\colon N\cdot C_{10}H_6\cdot NH_2$, which crystallises in red needles, m. p. 125°; this substance dissolves in concentrated sulphuric acid with production of an intense blue coloration. 2-Chloro-1-naphthyldiazonium chloride and β-naphthol yield 2-*chloro*-1-*naphthaleneazo-β-naphthol*, $C_{10}H_6Cl\cdot N\colon N\cdot C_{10}H_6\cdot OH$, which forms minute, red needles, m. p. 177°, and gives a bluish-violet coloration with concentrated sulphuric acid.

p-*Ethoxybenzeneazo-β-naphthol*, $OH\cdot C_{10}H_6\cdot N\colon N\cdot C_6H_4\cdot OEt$, crystallises in red needles, m. p. 132°; it dissolves in concentrated sulphuric acid, giving a reddish-violet coloration, and is reprecipitated on addition of water. 1-p-*Ethoxybenzeneazo*-2-*chloronaphthalene*,

$C_{18}H_{15}ON_2Cl$, crystallises in orange-yellow leaflets, m. p. 94°, and gives a violet coloration with concentrated sulphuric acid. R. V. S.

Behaviour of Some Nitroazo-derivatives Towards Phenylhydrazine. C. GASTALDI (*Gazzetta*, 1911, **41**, ii, 319—324. Compare Ponzio, Abstr., 1909, i, 443).—o-*Nitrobenzoylazobenzene*,

$$NO_2\cdot C_6H_4\cdot CO\cdot N\colon NPh,$$

is obtained by the action of nitrous anhydride on an ethereal suspension of *o*-nitrobenzoylphenylhydrazine; it crystallises in red needles, m. p. 89°, and is reduced by phenylhydrazine to *o*-nitrobenzoylphenylhydrazine.

m-Nitrobenzoylphenylhydrazine, $NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot NHPh$, is obtained by acting on an ethereal solution of phenylhydrazine with *m*-nitrobenzoyl chloride; it forms yellow laminæ, m. p. 158° (Autenrieth gave 205°; compare Abstr., 1901, i, 186).

m-*Nitrobenzoylazobenzene*, $C_{13}H_9O_3N_3$, crystallises in dark red laminæ, m. p. 117°, and is reduced to *m*-nitrobenzoylphenylhydrazine by phenylhydrazine.

p-*Nitrobenzoylazobenzene*, $C_{13}H_9O_3N_3$, forms small, red laminæ, m. p. 136°, and is similarly reduced by phenylhydrazine.

o-*Nitrobenzoyl*-p-*bromophenylhydrazine*,

$$NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot NH\cdot C_6H_4Br$$

(from *p*-bromophenylhydrazine and *o*-nitrobenzoyl chloride), crystallises in colourless needles tinged with yellow, and has m. p. 193°. When oxidised it gives o-*nitrobenzoylazo*-p-*bromobenzene*, m. p. 119—120°, which is, however, not pure.

m-*Nitrobenzoyl*-p-*bromophenylhydrazine*, $C_{13}H_{10}O_3N_3Br$, crystallises in pale yellow needles, m. p. 198°. m-*Nitrobenzoylazo*-p-*bromobenzene*, $C_{13}H_8O_3N_3Br$, forms bronze-coloured laminæ, m. p. 124°, and is reduced to *m*-nitrobenzoyl-*p*-bromophenylhydrazine by phenylhydrazine.

p-*Nitrobenzoyl*-p-*bromophenylhydrazine*, $C_{13}H_{10}O_3N_3Br$, crystallises in yellow needles, m. p. 194°. p-*Nitrobenzoylazo*-p-*bromobenzene*,

$$C_{13}H_8O_3N_3Br,$$

crystallises in bronze-coloured laminæ, m. p. 153°, and is reduced to *p*-nitrobenzoyl-*p*-bromophenylhydrazine by phenylhydrazine.

R. V. S.

Preparation of Bromonaphthalene-1-diazo-2-oxide-4-sulphonic Acid. CHEMISCHE FABRIK VORM. SANDOZ (D.R.-P. 236656).—When naphthalene-1-diazo-2-oxide-4-sulphonic acid is dissolved in concentrated sulphuric acid or chlorosulphonic acid, treated with bromine, and heated at 60—65°, bromination takes place, yielding *bromonaphthalene*-1-*diazo*-2-*oxide*-4-*sulphonic acid*, decomp. 180°; the *zinc* salt forms glistening, greenish-yellow needles.

F. M. G. M.

Nitrogen Chains: Diazohydrazides from Diazotetrazole. KARL A. HOFMANN and HEINRICH HOCK (*Ber.*, 1911, **44**, 2946—2956. Compare Abstr., 1910, i, 446, 547; this vol., i, 359).—Diazotetrazoleaminoguanidine (guanyltetrazyltetrazen),

$$NH\colon C(NH_2)\cdot NH\cdot NH\cdot N\colon N\cdot CN_4H,H_2O,$$

prepared as already described (Abstr., 1910, i, 446), crystallises in yellow, doubly refractive needles, is stable in air at 25—35°, and decomposes with slight explosion at 142°. It is acid to litmus, but dissolves in dilute nitric acid. It does not react with mercuric oxide or benzaldehyde, but Fehling's solution furnishes copper diazotetrazole (?) as a brown powder. Sodium hydroxide decomposes it into cyanamide, ammonia, and tetrazylazoimide. When heated with dilute sulphuric or nitric acid, cyanogen and nitrogen are evolved, and the residue contains aminoguanidine and its decomposition products, as well as aminotetrazolic acid. The *periodide*, $C_2H_7N_{10}I_2$, which forms brown to black, pleochroic, cubical crystals, explodes gently when heated, but very violently in contact with nitric acid and silver nitrate.

Diazotetrazole-semicarbazide, $NH_2\cdot CO\cdot NH\cdot NH\cdot N{:}N\cdot CN_4H,H_2O$, m. p. 122°, obtained by adding diazotetrazole to semicarbazide hydrochloride in aqueous solution in presence of sodium acetate, forms colourless, doubly-refractive crystals when dilute nitric acid is added to its solution in alkali. It is acid to litmus, and is only slowly decomposed by alkali, forming tetrazylazoimide and carbamide. The same products result from heating the substance with water or dilute acids.

The decompositions of these two substances are in harmony with the constitution assigned to them (compare Curtius, Abstr., 1893, i, 463; Wohl, Abstr., 1893, i, 509; Thiele and Marais, Abstr., 1893, i, 440).

Diazotetrazolebenzylideneaminoguanidine,

$$NH{:}C(NH_2)\cdot N(C_7H_6)\cdot N\cdot N{:}N\cdot CN_4H,$$

obtained by admixture of its components in acetic acid, is an orange-red substance, decomposes at 132°, and crystallises in groups of needles from alcohol by evaporation of its solution under reduced pressure. It is decomposed by acids, yielding nitrogen, cyanogen, benzaldehyde, and hydrazine. With concentrated sodium hydroxide solution it gives a *sodium* derivative, orange-red needles. *Diazotetrazolephenylhydrazide*, $NH_2\cdot NPh\cdot N{:}N\cdot CN_4H$, obtained by interaction of phenylhydrazine with diazotetrazole in acetic acid, separates from methyl alcohol on adding ether, in orange-red crystals, gives a brownish-red *sodium* derivative, and is decomposed by acids, yielding nitrogen, cyanogen, and phenylhydrazine. The mode of decomposition of these two compounds indicates that they are α-hydrazides, their behaviour with acids and alkalis clearly distinguishing them from the β-hydrazides represented by the first two (compare Wohl and Schiff, Abstr., 1900, i, 706).

Bisdiazotetrazolehydrazide, $HN_4C\cdot N{:}N\cdot NH\cdot NH\cdot N{:}N\cdot CN_4H$, obtained by adding hydrazine hydrochloride to diazotetrazole hydrochloride, both being in strongly cooled solution, occurs in doubly refractive spangles, and can be kept for a month in a desiccator at 25°, but explodes with great violence when pressed with a glass rod or heated to 90°. It is decomposed by acids, yielding nitrogen (5 atoms), cyanogen, ammonia, and tetrazylazoimide, but no hydrazine. Concentrated sodium hydroxide solution gives a *sodium* derivative, as intensely yellow, doubly refractive plates, which in water decomposes, giving nitrogen, tetrazylazoimide, and aminotetrazole, but no

ammonia. These reactions are in harmony with the constitution assigned to the substance, as are also its acid reaction and non-reactivity with benzaldehyde. With Fehling's solution gas is evolved, the solution becomes brownish-yellow, and, on warming, reddish-brown flocks are deposited, probably of a copper derivative or diazotetrazole.

Guanidine and dicyanodiamidine react with diazotetrazole to form salts of diazoaminotetrazolic acid (compare Abstr., 1910, i, 547). The *dicyanodiamidine* salt forms yellow groups of microscopic needles, and dissolves in sodium hydroxide solution, from which alcohol precipitates the *sodium* salt, $C_2N_{11}Na_3,H_2O$, doubly refractive, yellow needles. The well crystallised *barium* salt, $(C_2N_{11})_2Ba_3,8H_2O$, may be obtained from this by double decomposition. T. A. H.

A New Method of Preparing Diazoamino-compounds, and a New Reaction for Nitrous Acid. WILHELM VAUBEL (*Chem. Zeit.*, 1911, **133**, 1238).—Sodium nitrite, in aqueous solution, acts on the salts of aromatic amines with mineral acids to form diazoaminobenzene and its derivatives. Aniline hydrochloride and sodium nitrite yield diazoaminobenzene, the best yield of the latter being obtained when the proportions taken are 1 mol. of aniline hydrochloride and $\frac{1}{2}$ mol. of sodium nitrite. Hydrochlorides may be replaced by nitrates. Reaction proceeds more slowly when salts of different amines are mixed before addition of the nitrite.

A similar action occurs when solid sodium nitrite is added to an alcoholic solution of the amine salt, and also when the dry salts are intimately mixed. In these cases the reaction can easily become so violent that a portion of the diazoaminobenzene is decomposed.

The reaction may also be used in testing the presence of nitrites in water. The presence of 0·00035% of nitrite could be recognised by the yellow coloration formed on addition of aniline hydrochloride.

H. W.

Losses in the Isolation of Monoamino-acids [from Proteins] by the Ester Method. I. EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1911, **74**, 445—471. Compare Osborne and Breese Jones, Abstr., 1910, i, 598).—The isolation of the monoamino-acids obtained on hydrolysing proteins is not a quantitative operation. In the case of glutamic and aspartic acids, the yields obtained, starting from the pure acids, esterifying, and converting the ester into acid again, have been determined. The experiments have been carried out in a variety of ways, and the losses at each stage of the process determined by nitrogen determinations; for the details, the original should be consulted.

Starting from pure aspartic acid, about 40% is lost during the isolation by the ester method; with glutamic acid the loss is 30%. Glutamic acid is usually isolated without the help of the ester method, and the loss in this case will not be larger, but it is considered that the values for aspartic acid previously obtained can be doubled. E. F. A.

Ochrein. FRANCESCO MARINO-ZUCO and IDA FOA (*Gazzetta.*, 1911, **41**, ii, 331—336).—Ochrein is the name given by the authors to the

substance containing iron which is obtained when biotoxin acts on blood or hæmoglobin (compare Marino-Zuco and Giuganino, Abstr., 1910, ii, 223). It is prepared by incubating a sterile solution of biotoxin and oxyhæmoglobin for five or six days at 41°, until the absorption spectrum of hæmoglobin is no longer present, and the liquid does not become turbid on heating. The substance is an amorphous, ochre-coloured powder, insoluble in most solvents. The percentage composition of different samples is the same, and corresponds with the formula $C_{288}H_{508}O_{70}N_{79}Fe$. When heated with extremely dilute sodium hydroxide, a very small quantity of the substance dissolves, and the solution shows the spectrum which appears when biotoxin acts on blood (compare Marino-Zuco and Giuganino, *loc. cit.*). R. V. S.

3:5-Di-iodotyrosine from Iodised Protein. III. From Iodocasein. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, 74, 290—296).—3:5-Di-iodotyrosine was prepared from iodocasein, but the yield is small, namely, about 1%. Iodocasein contains 10—14% of iodine; of this, only 4—5% is united to tyrosine; the amount obtained represents only about one-tenth of the tyrosine present. W. D. H.

Composition of Different Kinds of Silk. XIII. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1911, 74, 427—428).—Silk from the cocoon of *Anapha* contained tyrosine, alanine, and glycine in large quantity, and was similar in composition to other kinds of silk. Silk from *Bombyx mori* and African tussore silk was also qualitatively similar.

Silks as a class are very similar in composition, all consisting mainly of tyrosine, alanine, and glycine. They are not, however, identical, showing differences in the nature and amount of their rarer constituents. E. F. A.

The Proteoses. EDGARD ZUNZ (*Bull. Acad. roy. Belg.*, 1911, 653—734).—The hetero- and prot-albumoses prepared by the methods of Pick, Adler, and Haslam, as well as the synalbumose and thioalbumose of Pick, were prepared in quantity, and a large number of both chemical and physical constants of the preparations were ascertained. The experimental methods are given in full detail, and the analytical results and physical constants are tabulated. Further separations were also attempted by the methods of ultra-filtration (Bechhold) and precipitation by colloids (Michaelis and Rona). It was found that the method of Pick yields products of the most constant composition, and his method of classification of the proteoses appears to be preferable to that suggested by Haslam, although it can be improved in certain details in the technique of precipitation introduced by Haslam. Certain differences in the physiological action of the fractions previously observed by the author are also summarised.
S. B. S.

Plastein Formation. A. RAKOCZY (*Zeitsch. physiol. Chem.*, 1911, 75, 273—281).—The Danilewski reaction is not due to the action of any specific substance, but plastein formation occurs in the case of all proteoclastic enzymes, rennet included. W. D. H.

Nomenclature of Enzymes. HANS VON EULER (*Zeitsch. physiol. Chem.*, 1911, 74, 13—14).—Enzymes are usually named after the substances they split, for instance, for example, maltase after maltose. This rule is difficult to apply to enzymes which produce syntheses. The suggestion made is that the termination in such cases should be *ese* instead of *ase*, for instance, lipase, lipese. W. D. H.

The Mode of Action of Phosphatese. HANS VON EULER and SIXTEN KULLBERG (*Zeitsch. physiol. Chem.*, 1911, 74, 15—28).—There is no evidence that the enzyme which synthesises carbohydrate phosphoric acid esters has any splitting action. The term *phosphatese* is suggested (see preceding abstract); it is active in faintly alkaline media, but its stability is small. The ester formed from dextrose and lævulose is optically inactive, and on decomposition by acids or bases yields no optically active products. The enzyme is found in yeast and *Aspergillus.* Two enzymes are really in all probability concerned, one which changes the dextrose or lævulose into an ester-forming carbohydrate, and the second is the phosphatese which builds together the carbohydrate and phosphate ions. W. D. H.

The Electrical Transport of Pepsin. CORNELIS A. PEKELHARING and WILHELM E. RINGER (*Zeitsch. physiol. Chem.*, 1911, 75, 282—289).—Using a commercial preparation of pepsin, Michaelis and Davidsohn (Abstr., 1910, i; 795) drew the conclusion that with acid of a certain strength, the pepsin travelled to both poles; on lessening the strength of acid, it went only to the cathode; with still weaker acid it again went to both poles, and finally with the weakest acid only to the anode. The preparation they used was mixed with proteoses. In the present research, the authors prepared their own pepsin from pig's stomach; they do not pretend it is absolutely pure, but at any rate it was free from any large admixture with grosser impurities. It always travelled to the anode; when, however, proteoses were added, it was carried more or less to the cathode also. No separation of pepsin from rennet occurred by this method. W. D. H.

The Influence of Hydrogen Ion Concentration on Trypsin Action. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1911, 36, 280—290).—The principles of the experiments and the methods of interpreting the results are precisely the same as those used by the authors in their investigations on the influence of hydrogen ion concentration on the action of invertin (next page). They draw the conclusion that trypsin is an amphoteric electrolyte existing in solution in the form of anions, cations, or unchanged molecules according to the [H˙] concentration. Only the cations act proteoclastically, and the trypsin action is directly proportional to the number of these present in solution. The acid dissociation constant is 5.10^{-7}. Above 10^{-8} the tryptic action diminishes, possibly owing to the formation of doubly charged inactive anions. The optimal action takes place therefore in solutions when [H˙] concentration $= 10^{-8}$.

S. B. S.

Preparation of Pure Invertase. REGINALD O. HERZOG (*Zeitsch. physiol. Chem.*, 1911, **74**, 511. Compare Euler and Kullberg, this vol., i, 825).—Polemical. Euler and Kullberg have ignored the measurements of the molecular weight of invertase from the diffusion constants made by Herzog and Kasarnowski (Abstr., 1908, i, 707).

E. F. A.

The Action of Hydrogen Ions on Invertin [Invertase]. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1911, **35**, 386—412).—The action of invertase on sucrose solutions was investigated in solutions with varying [H′] concentrations, and the zone of optimal action was found to occur between $[H'] = 0{\cdot}65 \times 10^{-5}$ and $0{\cdot}98 \times 10^{-3}$. A standard curve was obtained when x, the amount of change (estimated polarimetrically), was plotted against t, the time of action of the ferment, the curve being constructed from the various data obtained from certain closely agreeing experiments carried out under conditions of optimal ferment action. Another curve was constructed when the ratio T/t and log[H] were plotted against one another, T being the time necessary to produce a given change read from the standard curve, t being the actual time taken to produce that change in the concentration [H]. The form of the curve thus obtained is similar to that of the dissociation curve of weak acids obtained by Michaelis. The conclusions drawn from the result are, that invertase is an amphoteric electrolyte with acid dissociation constant $= 2 \times 10^{-7}$ and basic dissociation constant 10^{-12}. The inverting action on sucrose is due to the presence of undissociated electrolyte, its optimum action corresponding with its isoelectric point. As $k_a.k_b$ is greater than k_w, there is a broad isoelectric zone. Neither the cations nor the anions can act as ferments, and the action of the hydrogen ions depends, therefore, entirely on the degree of dissociation of invertase. The latter is not readily adsorbed by kaolin. Preliminary experiments on emulsin show that this is adsorbed to a greater extent than invertase.

S. B. S.

Influence of Certain Acids on the Inversion of Sucrose by Sucrase [Invertase]. FREDERICK STOWARD (*Bio-Chem. J.*, 1911, **6**, 131—140).—Acids favour the inversion of sucrose by invertase. The action proceeds most rapidly when small amounts of sulphuric, hydrochloric, nitric, and phosphoric acid are present, and also in the presence of larger amounts of acetic acid. Increase of acid beyond a certain concentration, which differs in the case of different acids, retards, and finally arrests, the action.

W. D. H.

Diastase. JÓSEF BURACZEWSKI, L. KRAUZE, and A. KRZEMECKI (*Bull. Acad. Sci. Cracow*, 1911, [*A*], **6**, 369—370).—Pure commercial diastase was treated in suspension in methyl alcohol with bromine or iodine. The compounds obtained contained 6·23% Br and 9·0% I respectively. When heated with water for half an hour, a greyish-white, insoluble substance, probably a halogenated protein, remained. The soluble portion was precipitated by alcohol, and behaved as a carbohydrate, giving a blue coloration with iodine like starch. Unchanged diastase converted it first into dextrin and then into reducing sugar;

mineral acids acted similarly. The carbohydrate gave the orcinol reaction. The phenylosazone obtained from the reducing sugar had m. p. 156—157°.

Diastase which has been boiled with very dilute mineral acids gives a blue coloration with iodine. It is regarded as an unstable compound of protein and a carbohydrate of the nature of starch, which is probably a pentosan. The araban described by Wroblewski as accompanying diastase is probably a dextrin-like decomposition product of this pentosan. E. F. A.

Action of Emulsin on Gentiopicrin in Alcohol. Émile Bourquelot and Marc Bridel (*J. Pharm. Chim.*, 1911, [vii], 4, 385—390).—It has generally been assumed that the activity of emulsin is inhibited by small quantities of alcohol (compare Bougarel, *Thèse*, Paris, 1877), but the authors find that emulsin still hydrolyses gentiopicrin to a slight extent even in presence of 95° alcohol.

In alcohol at 60°, gentiopicrin is hydrolysed to the extent of 77·2% in forty days, and the action then stops. In 80° alcohol the same equilibrium is reached in seventy-five days, whilst in 85° alcohol 69·1% is hydrolysed in the same time. In 90° alcohol action ceases at the end of fifty-three days, when 48·4% of the glucoside is decomposed, and in 95° alcohol no further hydrolysis takes place after the twentieth day, when 6 to 7% of the glucoside is hydrolysed.

Even after keeping ninety days in alcohol of 80° strength, emulsin is still active towards gentiopicrin, although its activity is diminished by this treatment.

Emulsin is insoluble in alcohol over 50° in strength, but with progressive dilution of the alcohol with water it becomes more soluble, and saturated, filtered limpid solutions of the enzyme in 10° or 20° alcohol are almost as active as similar solutions in water. In alcohols of strength above 50°, emulsin appears therefore to act by simple contact. T. A. H.

The Ricinus Lipase. Y. W. Jalander (*Biochem. Zeitsch.*, 1911, 36, 435—476).—The microscopic appearance of the mixture of fat and lipase in the presence of acetic acid and water vapour is described. The lipase imbibes water, and an emulsion is formed of the colloidal hydrated particles in oil (disperse phase). Details are given as to the methods for producing the oil–enzyme–acetic acid emulsion so as to obtain the maximum enzymatic activity. With 5 mg. enzyme (prepared by a modification of Nicloux's method) and 1 gram of triolein or cotton-seed oil, the best results are produced with about 0·6 c.c. of acetic acid. The concentration of the latter can vary between $N/500$ and $N/10$ without producing appreciable variations in the results. Much depends, however, on the mechanical treatment of the mixture, about which point full experimental details are given. The ricinus powder contains a small amount of acid which can be washed away. This washed powder in the presence of water alone is only slightly active. If it is first treated, however, with $N/10$-acid, it reaches its maximal activity in the presence of water alone. The results seem to indicate that a free acid plays the activating part in the enzyme action. By keeping the purified enzyme, however, for

some time with water or acid, its activity is diminished. The purified enzyme loses its activity when kept with neutral fats alone, without the presence of either acid or water. Of the fats investigated, triolein exerts the greatest action in this respect. In experiments lasting over one hour, the Schütz law $x/\sqrt{\epsilon}$ = constant (when x = amount saponified, ϵ = quantity of enzyme) was found to hold good over a comparatively large range. With more rapid hydrolysis, however, the law no longer held. The relationship between the time of action and the amount saponified was also investigated in numerous experiments. It was found that the relationship can be best expressed by the equation x/t^m = constant, when m varied between 0·57 and 0·70. No perfectly satisfactory formula could, however, be found. The lipase can also produce fats synthetically from oleic acid and glycerol. The presence of a small quantity of water, sufficient to produce the swelling of the lipase, accelerates the synthetical reaction, especially if the mixture be kept in continual rotation. S. B. S.

Synthesis of Fats by the Action of Enzymes. F. L. Dunlap and L. O. Gilbert (*J. Amer. Chem. Soc.*, 1911, 33, 1787—1791).—Experiments are described which show that the lipase of castor oil seed is capable of effecting the synthesis of fat by its action on a mixture of glycerol and oleic acid (compare Taylor, *Univ. California Pub.*, *Path.*, 1904, 1, 33, and Welter, this vol., i, 409). E. G.

Extraction of Zymase from Fresh Brewers' Yeast by Plasmolysis. P. Rinckleben (*Chem. Zeit.*, 1911, 35, 1149—1150).—Brewers' yeast was incubated with glycerol (25 c.c. to 400 grams yeast) at 25° for fifteen to forty hours, whereby the yeast was plasmolysed and the mass became liquid. By filtering through hardened filter-paper, a liquid was obtained which, as a rule, was without fermentative activity. In a few cases, however, the liquid readily fermented sugars, whilst in others it was only active after the addition of a boiled yeast-juice. The last cases thus owed their inactivity to a disappearance of the co-enzyme of alcoholic fermentation during the plasmolysis.

An active liquid was also obtained when yeast was plasmolysed by means of disodium hydrogen phosphate in the presence of boiled yeast-juice which had previously been dried in a vacuum.

W. J. Y.

p-Aminophenylarsine Tetraiodide. Aldo Patta and Piero Caccia (*Boll. Soc. Med.-Chirurg. Pavia*, 1911; Reprint, 9 pp. Compare Mameli and Patta, Abstr., 1909, i, 543; 1910, i, 531; also Bertheim, this vol., i, 593).—p-*Aminophenylarsine tetraiodide hydriodide*, $AsI_4 \cdot C_6H_4 \cdot NH_2,HI$, is obtained when *p*-aminophenylarsinic acid is heated with hydriodic acid (D 1·7) until iodine vapour is evolved in moderation; it forms orange-red crystals, m. p. 140°, and give a white, insoluble substance on treatment with water. The toxicity of this tetraiodide does not differ greatly from that of the atoxyl derivatives of Mameli and Patta (*loc. cit.*), but its injection produces a marked local action. R. V. S.

Preparation of Arsenophenols. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 235430. Compare Abstr., 1909, i, 347; 1910, i, 452).—The reduction of hydroxyarylarsinic acids has been previously described, and the preparation of halogenated derivatives is now recorded. When sodium *p*-hydroxyphenylarsinite is treated with sodium hypochlorite (or hypobromite) in aqueous solution at the ordinary temperature, and the solution acidified after twelve hours, the dihalogenated acid (accompanied by trihalogenated phenol) separates; it crystallises from water, and does not melt below 260°.

p-*Di-iodohydroxyphenylarsinic acid* is obtained when sodium *p*-hydroxyphenylarsinite (285 parts) is treated with potassium iodate (220 parts) in dilute sulphuric acid solution, heated at 100°, and potassium iodide (220 parts) subsequently added; on cooling the product separates in crystalline form.

Tetrachloroarsenophenol, a yellow powder insoluble in water, is prepared by treating the foregoing dichloro-acid with alkaline sodium hyposulphite in the presence of magnesium chloride at 50° for some time; the corresponding *tetrabromo-* and *tetraiodo-arsenophenols* can be analogously prepared, have similar properties, and are decomposed at 200° into arsenophenol. F. M. G. M.

Preparation of Aminohydroxyarylarsenious Oxides. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 235391. Compare Abstr., 1909, i, 148).—*Aminohydroxyphenylarsenious oxide* separates as a colourless, microcrystalline powder when a very dilute sulphuric acid solution of aminophenolarsinic acid (Abstr., 1909, i, 804) is treated with potassium iodide, saturated with sulphur dioxide at the ordinary temperature, and subsequently rendered alkaline with ammonium hydroxide; it is somewhat soluble in water, readily so in mineral acids and alkali hydroxides. F. M. G. M.

Nitro- and Amino-arsanilic Acids. ALFRED BERTHEIM (*Ber.*, 1911, 44, 3092—3098).—The toxicity of phenylarsinic acid is considerably diminished by the entrance of an amino-group into the benzene nucleus. A similar effect accompanies the introduction of a second amino-group, the toxicity of 3:4-diaminophenylarsinic acid being only one-twentieth that of *p*-aminophenylarsinic acid.

p-Oxalylaminophenylarsinic acid (D.R.-P. 231969),

$$CO_2H\cdot CO\cdot NH\cdot C_6H_4\cdot AsO(OH)_2,H_2O.$$

prepared by heating *p*-aminophenylarsinic acid or its sodium salt with oxalic acid, forms a white crystalline powder, consisting of short, microscopic prisms, which do not melt or decompose below 300°. On nitration, it yields 3-nitro-*p*-oxalylaminophenylarsinic acid, which forms almost colourless, short prisms, and is hydrolysed to 3-nitro-*p*-aminophenylarsinic acid, $NO_2\cdot C_6H_3(NH_2)\cdot AsO(OH)_2$. This crystallises in yellow needles, decomposing explosively above 300°; it is reduced by aqueous sodium hyposulphite to 3:4-*diaminophenylarsinic acid*, $C_6H_3(NH_2)_2\cdot AsO(OH)_2,\frac{1}{2}H_2O$, which forms small, colourless prisms, m. p. 158—159° (decomp.), with previous darkening at 140°.

Aziminophenylarsinic acid, $N{<}{\substack{N-\\ NH}}{>}C_6H_3\cdot AsO(OH)_2$, prepared by

the action of nitrous acid on diaminophenylarsinic acid, crystallises in stout, colourless prisms, decomposing explosively above 300°.

The diamino-acid reacts with carbonyl chloride, yielding o-*phenylenecarbamidearsinic* (*benziminazolonearsinic*) *acid*,

$$CO{<}^{NH}_{NH}{>}C_6H_3\cdot AsO(OH)_2,$$

which crystallises in prisms or platelets, and with phenanthraquinone in glacial acetic acid solution to form *diphenylenequinoxalinearsinic* (*phenanthraphenazinearsinic*) *acid*, $\begin{matrix}C_6H_4\cdot C{:}N \\ | \quad\quad | \\ C_6H_4\cdot C{:}N\end{matrix}{>}C_6H_3\cdot AsO(OH)_2$; both substances remain unchanged below 300°. F. B.

Preparation of Nitrohydroxyarylarsinic Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 235141).—When nitro-1-aminophenyl-4-arsinic acid (this vol., i, 594, 760) is stirred into a solution of potassium hydroxide (36 Bé) and heated at 80°, it yields the corresponding nitrophenol-4-arsinic acid, which is isolated by acidification, whilst by an analogous series of operations *o*-toluidine-4-arsinic acid furnishes nitro-*o*-cresol-4-arsinic acid. F. M. G. M.

Diphenylstibine Compounds. AUGUST MICHAELIS and ARWED GÜNTHER (*Ber.*, 1911, 44, 2316—2320).—The substance produced by the reaction of triphenylstibine with antimony trichloride in presence of xylene is not chlorophenylstibine, as stated by Hasenbäumer (Abstr., 1899, i, 209), but chlorodiphenylstibine, $SbPh_2Cl$, and certain of the derivatives obtained from it have been described previously by Michaelis and Reese (Abstr., 1886, 885).

Chlorodiphenylstibine, m. p. 68°, crystallises from ether on addition of light petroleum, decomposes when heated in air, but melts unchanged under water, and irritates the skin when applied to it. Sodium carbonate converts it into *diphenylstibine oxide*, $O(SbPh_2)_2$, m. p. 78°, which separates on evaporation of its solutions in alcohol as an oil, which slowly solidifies into colourless needles. Both these substances have faint odours in the cold, but develop strong, unpleasant odours when heated. The oxide is transformed into *diphenylstibine sulphide*, m. p. 69°, by hydrogen sulphide in alcohol; it crystallises from hot alcohol in long, colourless needles. T. A. H.

Preparation of Nuclear Substituted Mercury Derivatives of Halogenated or Nitrated Phenols, or Halogenated Nitrophenols. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 234851).—When halogen or nitro-derivatives of phenols are treated with mercuric oxide or mercuric salts, substitution products possessing both acidic and basic characters are formed; they can be purified by solution in alkali hydroxide and precipitation by carbon dioxide, and are decomposed by concentrated mineral acids into their generators.

p-*Chlorophenylmercuric oxide* was prepared by boiling *p*-chlorophenol with an aqueous acidified (sulphuric acid) solution of mercuric sulphate; o-*nitrophenylmercuric oxide*, a yellow powder, was prepared in an analogous manner, whilst 4-*chloro-2-nitrophenylmercuric oxide*, a yellow, crystalline powder, was obtained from mercuric oxide and 4-chloro-2-nitrophenol in boiling acetic acid solution. F. M. G. M.

INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

THE object of the abstracts of chemical papers published elsewhere than in the Transactions of the Society is to furnish the Fellows with a concise account of the progress of chemical science from month to month. It must be understood that as the abstracts are prepared for the information of the Fellows in general, they cannot possibly be made so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally.

2. Before beginning to write the abstract, the whole of the original paper must be read, in order that a judgment may be formed of its importance and of the scale on which the abstract should be made.

3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.

4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper.

5. The abstract should be made as short as is consistent with a clear and accurate statement of the author's results.

6. A concise statement showing the general trend of the investigation should be given at the commencement of those abstracts where the nature of the original permits of it.

7. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should, as a rule, be made of this fact.

8. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.

9. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned quite shortly. On the other hand, data such as melting and boiling points, sp. gr., specific rotation, &c., must be given in every case unless recorded in earlier papers.

Nomenclature.

10. Employ names such as *sodium chloride, potassium sulphate* for inorganic compounds, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chlorides, sulphurous and sulphuric acids.

11. Term compounds of metallic radicles with the OH-group *hydroxides* and not hydrates, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation.

12. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as sodium hydrogen sulphate, disodium hydrogen phosphate, &c., to the acid salts. Basic salts as a rule are best designated merely by their *formulæ.*

13. Names in common use for oxides should be employed, for example: NO, nitric oxide; CO_2, carbon dioxide; P_4O_{10}, phosphoric oxide; As_4O_6, arsenious oxide; Fe_2O_3, ferric oxide.

14. In open chain compounds, Greek letters must be used to indicate the position of a substituent, the letter α being assigned to the first carbon atom in the formula, except in the case of CN and CO_2H, for example, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2I$ α-iodobutane, $CH_3\cdot CH_2\cdot CH_2\cdot CN$ α-cyanopropane.

15. Isomeric open chain compounds are most conveniently represented as substitution derivatives of the longest carbon chain in the formula; for example,

$$\begin{matrix}CH_3\\ CH_3\cdot CH_2\end{matrix}\!>\!CH\cdot CH\!<\!\begin{matrix}CH_3\\ CH_3\end{matrix} \quad\text{or}\quad CH_3\cdot CH_2\cdot CHMe\cdot CHMe\cdot CH_3$$

should be termed $\beta\gamma$-dimethylpentane not methylethyl*iso*propylmethane, and $\begin{matrix}CH_3\\ CH_3\end{matrix}\!>\!CH\cdot CH\!<\!\begin{matrix}CH_3\\ CO_2H\end{matrix}$ or $CH_3\cdot CHMe\cdot CHMe\cdot CO_2H$ should be termed $\alpha\beta$-dimethylbutyric acid, not $\alpha\beta\beta$-trimethylpropionic, or α-methyl*iso*valeric, or methyl*iso*propylacetic acid.

16. Use names such as methane, ethane, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3\cdot[CH_2]_5\cdot CH_3$, &c. Term the hydrocarbons C_2H_4 and C_2H_2 ethylene and acetylene respectively (not ethene and ethine). Homologues of the ethylene series are to be indicated by the suffix *-ene*, and those of the acetylene series, wherever possible, by *-inene*. Adopt the name allene for the hydrocarbon $CH_2{:}C{:}CH_2$.

17. Distinguish all hydroxyl derivatives of hydrocarbons by names ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, or n-hydric, according to the number of OH-groups. Compounds which are not alcohols, but for which names ending in *ol* have been used, are to be represented by names ending in *ole*, if a systematic name cannot be given, thus anisole not anisol, indole not indol. Compounds such as MeONa, EtONa, &c., should be termed sodium methoxide, sodium ethoxide, &c.

18. The radicles indicated in the name of a compound are to be

given in the order fluoro-, chloro-, bromo-, iodo-, nitro-, nitroso-, amino-, imino-, cyano-, thiocyano-, hydroxy-, keto-.

19. Compounds analogous to the acids of the lactic series containing the OH-group should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups OEt, OPh, OAc, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus α-ethoxypropionic acid, $OEt\cdot CHMe\cdot CO_2H$, instead of ethyl-lactic acid; 3:4-diethoxybenzoic acid, $(OEt)_2C_6H_3\cdot CO_2H$, instead of diethylprotocatechuic acid; and α-acetoxypropionic acid, $OAc\cdot CHMe\cdot CO_2H$, instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, thus, $C_6HEt_2(OH)_2\cdot CO_2H$, and not $C_6H_3(OEt)_2\cdot CO_2H$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2\cdot CO_2H$.

20. The term *ether* should be restricted to the oxides of hydrocarbon radicles and their derivatives, and the esters (so-called compound ethers or ethereal salts) should be represented by names similar to those given to metallic salts.

21. When a substituent is one of the groups NH_2, NHR, NR_2, NH or NR, its name should end in *ino*; for example, β-aminopropionic acid, $NH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, β-anilino-acrylic acid, $NHPh\cdot CH\colon CH\cdot CO_2H$, α-iminopropionic acid, $NH\colon CMe\cdot CO_2H$.

22. Compounds of the radicle SO_3H should, whenever possible, be termed sulphonic acids, or failing this, sulpho-compounds; for example, benzenesulphonic acid, sulphobenzoic acid.

23. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteins, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

24. The Collective Index, 3rd decade (1893–1902) should be adopted as the standard of reference on questions of nomenclature not provided for in the preceding sections.

Notation.

25. In empirical formulæ the elements are to be given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

26. Equations should be omitted unless essential to the understanding of the results; as a rule, they should not be written on a separate line, but should "run on" with the text.

27. To economise space, it is desirable:

(a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula.

(b) That formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^α for $CH_2{\cdot}CH_2{\cdot}CH_3$, Pr^β for $CH(CH_3)_2$, Ph for C_6H_5, Py for C_5H_4N, Ac for $CO{\cdot}CH_3$, and Bz for $CO{\cdot}C_6H_5$.

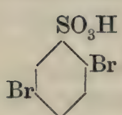
(c) That formulæ should be written *in one line* whenever this can be done without obscuring their meaning.

28. In representing the constitution of benzene derivatives, the relative positions of the radicles in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

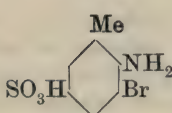
(a) The abbreviations *o*-, *m*-, and *p*-, should be used in place of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or para.

(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radicle of each of these parent substances is to be regarded as in position 1 (compare Collective Index).

(c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed; for example :—

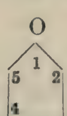


is 2 : 5-dibromobenzenesulphonic acid ;

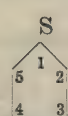


is 3-bromo-*o*-toluidine-5-sulphonic acid.

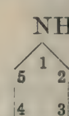
29. In representing the constitution of derivatives of other "closed chain" hydrocarbons, graphic formulæ should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (3rd edition, 1910, pp. 14—26) should be used, of which the following schemes may be regarded as typical :—



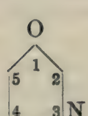
Furan.



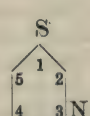
Thiophen.



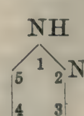
Pyrrole.



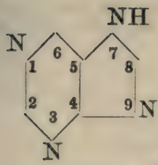
Oxazole.



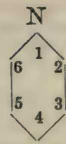
Thiazole.



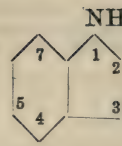
Pyrazole.



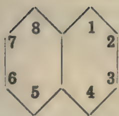
Purine.*



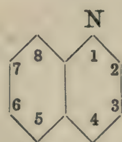
Pyridine.



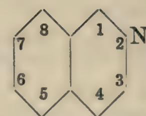
Indole.



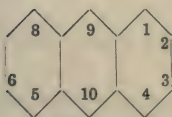
Naphthalene.



Quinoline.

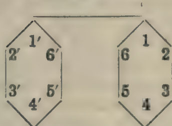


*iso*Quinoline.

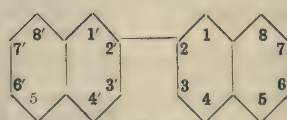


Anthracene.

Phenanthrene.



Diphenyl.



ββ-Dinaphthyl.

Manuscript.

30. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts cannot be accepted unless written on quarto paper (10 × 8 in.).

31. Not more than one abstract must appear on a sheet.

32. When an abstract exceeds a sheet in length, the sheets must be fastened together by means of gum at the top left-hand corner.

33. The name of the abstractor must be written diagonally at the top left-hand corner of the first sheet of the abstract.

Proofs.

34. Abstractors are expected to read and correct proofs carefully, and to check all formulæ and figures against MSS.

35. All proofs, however small, must be returned to the Sub-Editor not later than 24 hours after receipt from the printers.

***** The Editor's decision, in all matters connected with the Abstracts, must be considered final.**

* This numbering, proposed originally by E. Fischer, is adopted in the text of the *Lexikon*.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

All references to Journals should give the abbreviated title, the year of publication, the series, the volume and the page; thus *Ber.* 1901, **34**, 2455; *Bull. Soc. chim.* 1901, [iii], **25**, 794; *Gazzetta* 1901, **31**, i, 554.

ABBREVIATED TITLE.	JOURNAL.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Physik	Annalen der Physik.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arch. expt. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Hygiene	Archiv für Hygiene.
Arch. Néerland.	Archives Néerlandaises des sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
* *Bied. Zentr.*	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Boll. chim. farm.	Bollettino chimico farmaceutico.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci., St. Pétersbourg.	Bulletin de l'Académie Impériale des Sciences de St. Pétersbourg.
Bull. Assoc. chim. Sucr. Dist.	Bulletin de l'Association des chimistes de Sucrerie et de Distillerie.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. ind. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
* *Chem. Zentr.*	Chemisches Zentralblatt.
Chem. News	Chemical News.
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.

* Abstracts from the *Zentralblatt* are made only in the case of papers published in journals other than those included in this list.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Exper. Stat. Record	Experiment Station Record.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
Jahrb. Radioaktiv. Elektronik.	Jahrbuch der Radioaktivität und Elektronik.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Chim. phys.	Journal de Chimie physique.
J. Geol.	Journal of Geology.
J. Hygiene	Journal of Hygiene.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Landw.	Journal für Landwirtschaft.
J. Med. Research	Journal of Medical Research.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Soc. New South Wales.	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers	Journal of the Society of Dyers and Colourists.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
K. Svenska Vet-Akad. Handl.	Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Lancet.	The Lancet.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Le Radium	Le Radium.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Eng. Kyōtō.	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Metallurgie	Metallurgie.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nuovo Cim.	Il Nuovo Cimento.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zeit.	Pharmazeutische Zeitung.
Pharm. Zentr-h.	Pharmazeutische Zentralhalle.
Philippine J. Sci.	Philippine Journal of Science.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. exp. Physiol.	Quarterly Journal of experimental Physiology.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche-Napoli.
Rev. de Métallurgie	Revue de Métallurgie.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U.S.A.
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U.S.A.
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wiss. Abhandl. Phys.-Tech. Reichsanstalt.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Biol.	Zeitschrift für Biologie.
Zeitsch. Chem. Ind. Kolloide.	Zeitschrift für Chemie und Industrie der Kolloide.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. prakt. Geol.	Zeitschrift für praktische Geologie.
Zeitsch. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Zeitsch Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

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